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FUELS AND LUBRICANTS FOR AIRCRAFT

M. E. Reznikov

Foreign Technology Division
Wright-Patterson Air Force Base, Ohio

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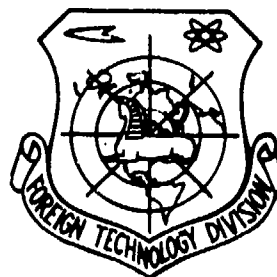
FOREIGN TECHNOLOGY DIVISION



FUELS AND LUBRICANTS FOR AIRCRAFT

by

M. Ye. Reznikov



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Г г	Г г	G, g	У у	У у	U, u
Д д	Д д	D, d	Ф ф	Ф ф	F, f
Е е	Е е	Ye, ye; E, e*	Х х	Х х	Kh, kh
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З з	З з	Z, z	Ч ч	Ч ч	Ch, ch
И и	И и	I, i	Ш ш	Ш ш	Sh, sh
Й й	Й й	Y, y	Щ щ	Щ щ	Shch, shch
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М м	М м	M, m	Ь ь	Ь ь	"
Н н	Н н	N, n	Э э	Э э	E, e
О о	О о	O, o	Ю ю	Ю ю	Yu, yu
П п	П п	P, p	Я я	Я я	Ya, ya

*ye initially, after vowels, and after u, ы; e elsewhere.
When written as ъ in Russian, transliterate as yë or ë.
The use of diacritical marks is preferred, but such marks may be omitted when expediency dictates.

GREEK ALPHABET

Alpha	Α α	α	Nu	Ν ν	ν
Beta	Β β	β	Xi	Ξ ξ	ξ
Gamma	Γ γ	γ	Omicron	Ο ο	ο
Delta	Δ δ	δ	Pi	Π π	π
Epsilon	Ε ε	ε	Rho	Ρ ρ	ρ
Zeta	Ζ ζ	ζ	Sigma	Σ σ	ς
Eta	Η η	η	Tau	Τ τ	τ
Theta	Θ θ	θ	Upsilon	Υ υ	υ
Iota	Ι ι	ι	Phi	Φ φ	φ
Kappa	Κ κ	κ	Chi	Χ χ	χ
Lambda	Λ λ	λ	Psi	Ψ ψ	ψ
Mu	Μ μ	μ	Omega	Ω ω	ω

RUSSIAN AND ENGLISH TRIGONOMETRIC FUNCTIONS

Russian	English
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sin	sin
cos	cos
tg	tan
ctg	cot
sec	sec
cosec	csc
sh	sinh
ch	cosh
th	tanh
cth	coth
sch	sech
esch	csch
arc sin	sin ⁻¹
arc cos	cos ⁻¹
arc tg	tan ⁻¹
arc ctg	cot ⁻¹
arc sec	sec ⁻¹
arc cosec	csc ⁻¹
arc sh	sinh ⁻¹
arc ch	cosh ⁻¹
arc th	tanh ⁻¹
arc cth	coth ⁻¹
arc sch	sech ⁻¹
arc esch	csch ⁻¹

rot	curl
lg	log

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M. Ye. Reznikov

FUELS AND LUBRICANTS FOR AIRCRAFT

V. G. Stolyarov, Editor

Moscow, 1973

INTRODUCTION

The tactical technical indices and operational reliability of aircraft depend on the composition and quality of the fuels, oils, lubricants, and technical fluids to a greater extent than those of any other hardware. The military might of rocket-armed air forces and the enormous scale of aviation transport are largely due to the advances of Soviet science and industry in the area of development and production of fuels and lubricants. Thanks to the close attention of the Communist Party and Soviet Government, the rapid development of aeronautical and rocket engineering is strengthened by a steady growth and improvement of the fuel base that it requires.

The founder of the Communist Party and Soviet State, V.I. Lenin, concerned about organizing the Red Air Force under the adverse conditions of a civil war, did not lose sight of the problems of supplying airplanes with fuel. Personally and through the authorities of the young Soviet Republic, Vladimir Il'ich enlisted the participation of leading scientists and engineers who had come over to the side of the revolution in building an air force and producing the fuel for it. Their scientific ideas were taken up and developed by thousands of science and engineering enthusiasts who were directed by the Party into aeronautics, aircraft construction, and the petroleum and chemical industries.

Continuing their traditional attitude toward practical applications, initiated in the area of petroleum refining by the luminary of Russian science D.I. Mendeleev, Soviet scientists provided successful solutions to the problems

of aviation and rocket fuels and lubricants. Back in 1918, near Moscow, N.D. Zelinskiy set up the production of gasoline for the fledgling Soviet aviation on the basis of the catalytic cracking process he proposed [89]¹. The laws of chain reactions discovered by N.N. Semenov in the 1920's were applied by the scientists of his school to the processes taking place in aircraft engines, and thus the requirement for the fuel of such engines could be determined. K.E. Tsiolkivskiy advanced the guiding concepts in the area of selection of propellants and oxidizers for rocket engines (he also considered it possible to use free radicals and nuclear energy in such engines). Back in the 1930's, scientists and experts at the Scientific Research Institute of Jet Propulsion and students who carried on this research developed and tested specific fuel compositions which form the basis of modern rocketry [56]. N.P. Petrov's fundamental ideas (in the 1880's) in the area of friction and lubrication, developed and perfected on the basis of modern advances in physics and chemistry, made it possible to determine the composition and provide for the necessary properties of lubricants of aircraft friction parts operating under complex conditions.

The present period has been characterized by the formation of a special branch of science concerned with the physical and chemical processes in engines, determined by the fuels and oils used therein - a science dealing with the application of fuels and lubricants (a leading Soviet expert in this area, Prof. K.K. Papok, proposed the name of chemomotology for this science). Its objective is to investigate and match fuels with oils, on the one hand, and with engines (their design and parameters, materials, operating conditions

¹Numbers in square brackets denote the bibliographic references at the end of the book.

on the other. Increasingly new and complex problems arise in connection with the development of jet propulsion technology, with the prodigious increase in velocity, altitude, range and duration of flight, and with increase in mechanical and thermal stresses on the engines and aircraft systems. Severe flight conditions cause irreversible changes in the composition and properties of fuels, lubricants, and technical fluids, which may thus cause malfunctions, engine and system failures, and destruction of individual parts and units [35].

In view of the dangerous aftereffects of failures, ensuring the reliability of aircraft is always problem No. 1. For this reason, the greatest emphasis is placed on the service properties of the fuels, lubricants and fluids on which the reliability of aircraft engines and systems depends: increasing the thermal stability, decreasing carbon scale formation, reducing the corrosive activity, improving the antiwear properties, etc. There is always the problem of improving the efficiency of fuels and lubricants, since each excess kilogram of fuel, oil, or fluid lifted by an aircraft correspondingly decreases the payload or the military capability of the aircraft.

The continuous progress in the quality of fuels and lubricants does not in any way reduce the acuteness of these problems, since the rapid development of aeronautics, cosmonautics, and rocketry requires the solution of even more complex problems and is the source of new contradictions and growth difficulties which must be overcome. At the same time, the negative effect of certain properties of a fuel or oil, unsatisfactory under particularly severe conditions, have to be offset by structural and technological measures. In the aircraft-fuel (or oil) system, everything is interrelated. While an insufficiently high

quality of the fuel (or oil) reduces the efficiency and reliability of an aircraft, raising the requirements imposed on the fuel (or oil) will cause the latter to become more expensive and will reduce the possibilities of their mass production, i.e., may lead to a nonprofitable technology or to the impossibility of providing it with the necessary quantity of fuel (or oil).

The gigantic plans for the development of the petroleum and chemical industries and refining of petroleum and gas, drawn up by the 26th Congress of the CPSU, provide for the possibility of production of all types and grades of fuels, lubricants and special fluids required by aircraft technology.

Part 1

FUELS

CHAPTER 1

GENERAL CHARACTERISTICS OF AIRCRAFT FUELS

Uses and Classification of Fuels

Basic Concepts

Internal combustion engines used in aircraft generate a thrust force by converting thermal energy. Substances consumed in the generation of thermal energy are called fuels. In the engines, this energy is converted with the aid of a gaseous mass carrier into mechanical work of ejection of a gas jet or rotation of a propeller.

The liberation of energy by the fuel may take place as a result of chemical or nuclear processes; the fuels are correspondingly divided into chemical and nuclear ones. Ordinary chemical fuels (kerosene, gasoline, etc.) liberate energy during combustion, which is a rapid oxidation process. Combustion requires not only a combustible, but also an oxidizer. In jet and piston engines, (JE and PE), the oxidizer is atmospheric air. The fuel for these engines contains no oxidizer; it consists only of the combustible substance. The terms "propellant" and "fuel" as applied to these engines are equivalent. Air is not

considered an integral part of the propellant, since it is supplied from the outside, and is not consumed from inside the aircraft.

Rocket engines do not require an outside oxidizer. As a rule, in liquid rocket engines, the oxidizer is a separate substance (liquid oxygen or nitric acid, etc.), which is loaded into the aircraft together with the combustible. In this case, the concepts of "propellant" and "fuel" are not equivalent; the propellant consists of two components, the combustible and the oxidizer. Rocket engines also use one-component propellants (monopropellants), mainly solids whose composition includes the oxygen necessary for combustion. Occasionally, the monopropellant used is a substance that does not burn, but decomposes with the evolution of heat (for example, hydrogen peroxide, hydrazine). These are also chemical fuels, since their evolution of energy is due to chemical reactions of recombination of atoms into molecules more stable than the initial ones.

In addition to their main purpose, to liberate energy, the fuel usually also acts as the source of the working substance, i.e., of the gas mixture which performs the work of the engine. The chief source of the mass carrier in jet and piston engines is air; the fuel and products of its combustion constitute only a minor part of the working substance. In rocket engines, the working substance is entirely made up of the propellant.

In many engines, liquid fuel is additionally used to cool the components and parts, to cool the oil, and for hydraulic control of various units [60, 81, 97]¹

¹Hereinafter, at the end of each subsection, numbers in brackets denote the literature references listed at the end of the book.

Composition of Fuels for Jet Engines

A typical classification of aircraft fuels, compiled on the basis of a systematization of data on the composition of modern and prospective fuels designed for various engines, is given in Fig. 1.

The majority of modern aviation fuels for jet and piston engines are liquid hydrocarbon mixtures obtained by refining petroleum. They are usually distinguished according to boiling temperatures; aviation gasoline boils in the range of approximately 140-180°C, aviation kerosene at 120-280°C, and heavy kerosene, at 200-315°C. Also used are wide-fraction fuels, i.e., mixtures of gasoline and kerosene.

Prospective¹ fuels for jet engines are considered to be liquefied hydrocarbon gases, pure synthetic hydrocarbons, and liquid hydrogen; less probable but fundamentally possible is the use of hydrides, i.e., compounds of hydrogen with other elements (boranes, hydrazine, ammonia), alcohols, suspensions and organic compounds of metals (aluminum, magnesium, etc.). In comparison with petroleum fuels, some of them yield more heat per unit weight or volume of fuel, while others, per unit of the amount of air pumped through the engine [10, 35, 60, 73, 81].

Composition of Rocket Propellants

All the enumerated substances, beginning with hydrocarbons, are used as the combustible component of propellants for liquid rocket engines. Abroad,

¹In Fig. 1, the connecting lines to prospective fuels are dashed lines.

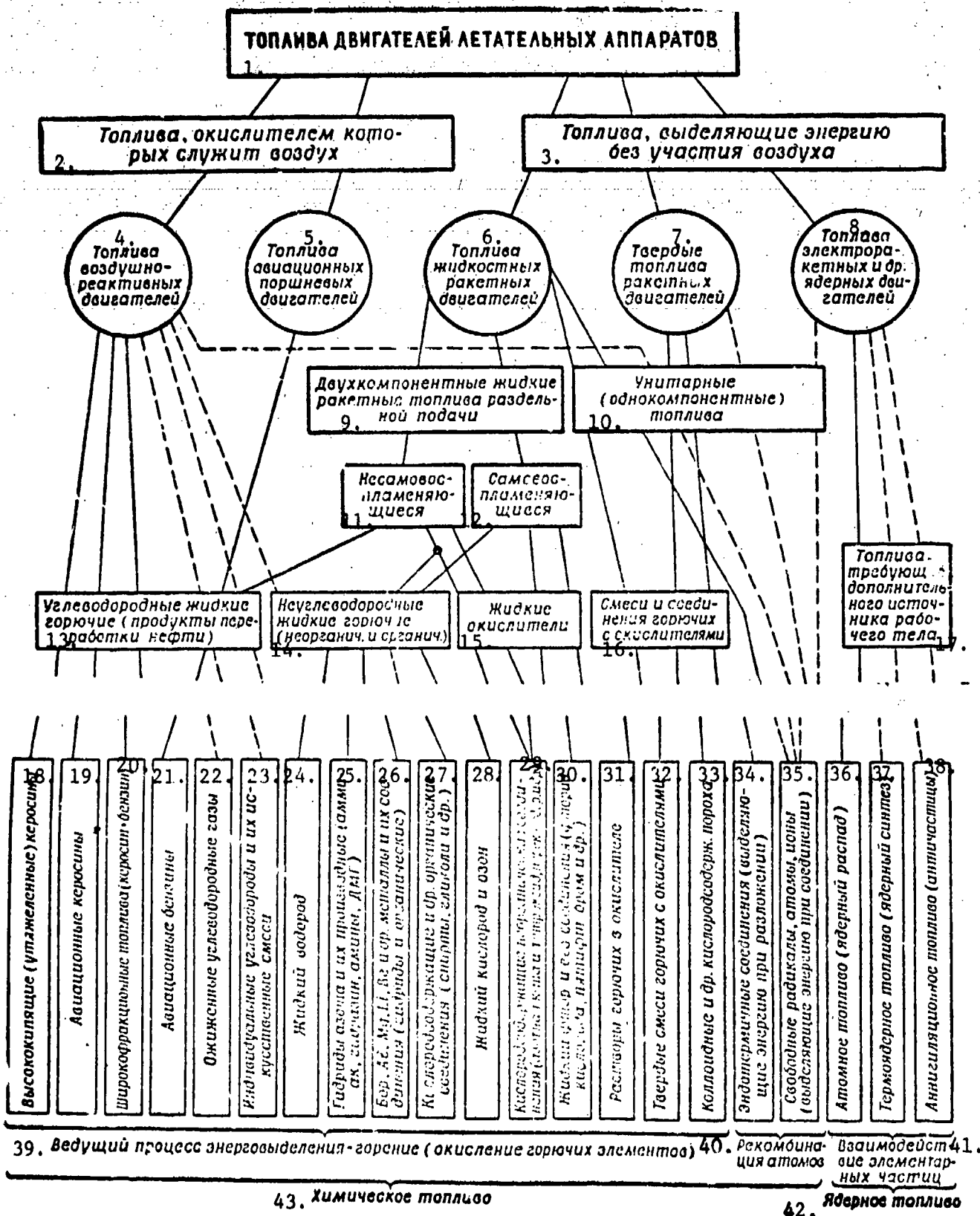
hydrides of nitrogen and their organic derivatives as well as liquid hydrogen have assumed a leading role in recent years. The oxidizing component of these propellants may be liquid oxygen and oxygen-containing compounds capable of giving up considerable quantities of oxygen to oxidize the fuel. Liquid fluorine and its compounds are considered to be prospective oxidizers. Liquid oxygen-based propellants are in the category of propellants which do not self-ignite when the engine is started, while liquid fluorine-based propellants are in the self-igniting category. Propellants based on oxygen-containing oxidizers belong to one or the other category, depending on the specific composition of the combustible component.

Monopropellants include, first, mixtures or solutions of fuel and oxidizer stable under storage conditions; secondly, substances whose molecular composition includes oxygen, which provides for their combustion; thirdly, so-called endothermic substances which absorb energy when they are formed from the elements and correspondingly evolve it on decomposing [9, 29, 38, 55, 73, 86, 90, 91].

New Energy Sources

Attempts are being made to develop a special type of chemical propellant for jet and rocket engines that liberates energy as a result of combination of free atoms and radicals (molecular fragments). Finally, a separate group of prospective propellants suitable chiefly for electric rocket engines consists of ordinary atomic fuel based on decaying isotopes of uranium and plutonium, used in stationary and naval nuclear reactors, and thermonuclear fuel based on the synthesis of deuterium, tritium, etc. [47, 55, 73, 119, 131].

Fig. 1. Classification of aircraft and rocket fuels.



Caption for Fig. 1

Fig. 1. Classification of aircraft and rocket fuels. Key:

1. Fuels for aircraft and rocket engines; 2. Fuels with air as oxidant;
3. Fuels liberating energy without the use of air; 4. Fuels for air-breathing engines; 5. Fuels for piston aircraft engines; 6. Propellants for liquid rocket engines; 7. Solid propellants for rocket engines;
8. Fuels for electric-rocket and other nuclear engines; 9. Liquid bipropellants; 10. Monopropellants (one-component propellants); 11. Non-self-igniting; 12. Self-igniting; 13. Hydrocarbon liquid fuels (petroleum-refining products); 14. Nonhydrocarbon liquid fuels (inorganic and organic); 15. Liquid oxidizers; 16. Mixtures and compounds of fuels with oxidizers;
17. Propellants requiring an additional source of working substance; 18. High-boiling (heavy) kerosenes; 19. Aviation kerosenes; 20. Wide-cut fuels (kerosene + gasoline); 21. Aviation gasolines; 22. Liquefied hydrocarbon gases;
23. Pure hydrocarbons and their artificial mixtures; 24. Liquid hydrogen;
25. Nitrogen hydrides and their derivatives (ammonia, hydrazine, amines, DMH); 26. Boron, Al, Mg, Li, Be and other metals and their compounds (hydrides and organic); 27. Oxygen-containing and other organic compounds (alcohols, glycols, etc.); 28. Liquid oxygen and ozone; 29. Oxygen-containing inorganic compounds (nitric acid and nitrogen tetroxide, hydrogen peroxide, etc.); 30. Liquid fluorine and its compounds (oxygen fluoride, bromine pentafluoride, etc.); 31. Solutions of fuels in oxidizer; 32. Solid mixtures of fuels and oxidizers; 33. Colloidal and other oxygen-containing powders; 34. Endothermic compounds (evolving energy on decomposing; 35. Free radicals, atoms, ions (evolving energy on combining); 36. Atomic fuel (nuclear fission); 37. Thermo-nuclear fuel (nuclear fusion); 38. Annihilation fuel (antiparticles); 39. Prime energy-producing process - combustion (oxidation of combustible elements); 40. Recombination of atoms; 41. Interaction of elementary particles; 42. Nuclear fuel; 43. Chemical fuel.

PROCESSES OF IGNITION AND COMBUSTION OF FUEL

Nature of Combustion

Combustion of ordinary fuel is a fast oxidation reaction in which the chemical energy of the fuel is converted mainly into thermal energy, and the fuel itself is converted mainly into gaseous products. The combustible elements in the composition of most modern fuels are carbon and hydrogen. In addition, the composition of certain rocket fuels includes aluminum, magnesium,

boron, beryllium, and lithium as their combustible elements. Oxidation consists essentially in the transfer of valence (outer) electrons from atoms of the combustible element to atoms of the oxidizer element. Thus acquiring a positive charge, the atoms of combustible are attracted to the negatively charged atoms of the oxidizer element, for example, oxygen or fluorine, and form molecules of oxidation products - carbon dioxide CO_2 , water vapor H_2O , hydrogen fluoride HF , etc.

Chain oxidation reactions. They consist of a series of repeating units in the course of which active particles, i.e., free atoms and radicals, are formed. A negligible small amount of active intermediate products is sufficient for a continuous chain transformation which involves a large mass of the initial substances (for example, hydrocarbon and oxygen), unit by unit. In order for oxidation to take place in the form of combustion, conditions must exist for rapid displacement of the active particles and branching of chains of the reactions. Such conditions exist only in a gaseous medium and not in liquids and solids. Liquid fuel is first converted into steam, while solid fuel decomposes, forming vapor and gases (is gasified) which then burn. For example, kerosene practically does not vaporize up to $28-30^\circ\text{C}$, and hence is not ignited by a flame. In order for a fuel to burn, it is necessary to create favorable conditions for its vaporization or gasification. Such conditions may be created when the surface of a liquid or solid fuel is heated by the combustion zone of gases, by an external source, or as a result of exothermic reactions within the fuel itself [23, 46, 52, 88, 94].

Ignition

The combustion of a mixture is excited by chemically active particles possessing a sufficient energy for breaking the chemical bonds of the atoms in the molecules of combustible and oxidizer. Active particles are formed on intense heating of the combustible mixture by an electric spark or an incandescent surface, or by an abrupt compression or some other method. For inflammation to occur, it is necessary that the rate of liberation of heat due to exothermic reactions in an initially heated volume of mixture (inflammation center) exceed the rate of heat transfer to the ambient space. The evolution of heat in the inflammation center is proportional to the volume, and the transfer is proportional to its surface area; the size of the center is proportional to their ratio. The lower the chemical activity and calorific capacity of the mixture, the larger the initial ignition kernel necessary for its kindling [46, 75, 88, 94].

Flame Propagation

Following ignition, the normal flame propagation in a quiescent noneddying mixture takes place at a rate of 10-30 cm/sec (laminar combustion). The layer of fresh mixture in contact with the flame is heated to 1500-3000°C and above (the temperature depends on the composition of the gaseous mixture), is chemically activated by the flow of active particles, and ignites. The thickness of the flame zone is of the order of 0.1 mm or less.

The rate of high-temperature chemical reactions (w) is sharply (exponentially) dependent on temperature; according to Arrhenius' law

where E is the activation energy that must be imparted to the gas in order for a given reaction to occur;

R is the gas constant;

T is the absolute temperature.

This promotes the contraction of the combustion zone into a surface, i.e., into a thin front of qualitative discontinuity in which in addition to a sharp temperature rise, there takes place a sharp transition of the gas composition from the initial combustible mixture to the combustion products, associated with the liberation of heat. The time of this transition is of the order of a millisecond or less. The temperature rise causes a local increase (in the thin layer) in the rate of the reaction and of liberation of heat, which in turn provides for the maximum temperature increase possible in a given chemical transformation.

The motion of the gas in the engine combustion chamber multiplies the flame propagation rate many times over. The flame is vigorously driven into the fresh mixture by the sharply expanding hot combustion products, its front is distorted by turbulent velocity pulsations, and the separate combustion kernels are propelled forward by the pulsations (relay flame propagation). On the sinuous combustion surface, increased by the relay kernels, many times more of the combustion mixture burns during the same period of time than could burn on a smooth flame front. In addition, small-scale velocity pulsations increase the number of molecular collisions. Ultimately, the rate of turbulent combustion reaches 20-40 m/sec [21, 46, 52, 94, 114].

Diffusion Combustion

The zone of combustion of the fuel injected into the chamber usually constitutes a spatially diffuse flame with a complex internal structure consisting of alternating regions of vaporized fuel (combustible), pure air (or oxidizer vapor) and combustion products, which become mixed together. Such a flame is referred to as a diffusion flame. The "surface" mechanism of combustion is apparently retained under these conditions also. Actual regions of combustion spontaneously contract into thin layers (by virtue of Arrhenius' law) wherever the mixed gases generate the maximum temperature rise during combustion. The rate of the combustion reactions is then determined by the rate of transfer of combustible vapor and air (or oxidizer vapor) to the combustion surface and depends little on the chemical properties of the fuel [21, 52, 114].

Chemical Mechanism of Combustion

Despite the enormous number of studies in this field, the chemical mechanism of combustion remains largely unclear for hydrocarbon fuels. The main approach to high temperature oxidation of hydrocarbon fuels consists in studying the chain processes of formation and decomposition of gaseous intermediate products (peroxides, aldehydes, etc.) at relatively low temperatures and in extrapolating these processes to the region of high temperatures according to Arrhenius' law - formula (1.1). However, this approach does not account for certain practically important phenomena: the presence of solid phase hydrocarbons in the flame, i.e., minute particles of pure carbon (soot) measuring tenths

or hundredths of a micron, and the phenomena of smoking and carbon deposition. If the soot burns and none remains in the end product of combustion, it shows up in a sharp (severalfold) increase in flame radiation energy and in a strong electron emission. The heat and electron radiation of a hydrocarbon flame is as intense as if it were a solid, not a gaseous mixture.

Judging from its radiation intensity, the concentration of soot in a flame depends on the fraction of carbon in the hydrocarbon and even more on the structure of the hydrocarbon skeleton of the molecules. The two-phase character of a hydrocarbon flame may not be a random phenomenon, contrary to views held until recently, but an essential stage of the process of combustion of hydrocarbons. In particular, the course of the process may be represented¹ as consisting of dehydrogenation (pyrolysis) of hydrocarbon molecules with the formation of free hydrogen, carbon vapor, and in part, products of their intermediate oxidation, then condensation of the carbon vapor into soot upon its supersaturation, and finally, combustion of the soot, hydrogen and intermediate oxidation products [46, 52, 113, 114].

Carbon Deposition

At a high concentration of soot in the flame, the soot may deposit on the combustion chamber walls and its parts. Dense carbon scale is sometimes formed, apparently due to thermal decomposition and oxidative condensation of the liquid phase of the fuel, i.e., droplets fallen on a solid surface. Carbon deposition increases if the liquid fuel is thrown by eddies onto the walls and parts of the combustion chamber, and also if the vaporizability of the fuel is poor.

¹Author's point of view.

The greatest tendency to form soot and carbon deposits is manifested by aromatic hydrocarbons, whose molecules contain a compact, difficult-to-decompose group of six carbon atoms, and particularly bicyclic aromatic hydrocarbons with an even more compact grouping of ten carbon atoms [7, 58, 73].

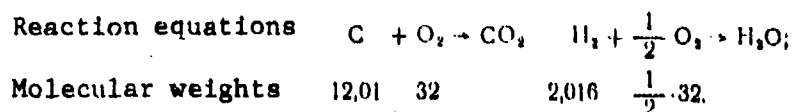
Detonation

When the chemical activity of a combustible mixture is high, the combustion may assume the character of detonation (explosion): supersonic pressure shock waves are formed in the burning mixture, and the flame velocity increases sharply (up to several hundred or even thousand meters per second). A detonation (explosion) wave represents the joint propagation of a compression shock wave, which causes the fuel to self-ignite, and of waves of combustion, which is sustained by the energy evolved. In detonation, the temperature in the reaction zone is higher than in normal combustion. Detonation gives rise to thermal and mechanical loads which are unsafe for engines [52, 94, 113].

AMOUNT OF OXIDIZER REQUIRED

Stoichiometric Coefficient of the Elements

The amount of oxygen theoretically required for the complete oxidation of the combustible elements can be determined from the equations of the oxidation reactions. Thus, for carbon and hydrogen:



Consequently, 1 kg of carbon consumes $32:12.01=2.66$ kg of oxygen, and 1 kg of hydrogen consumes $16:2.016=7.94\approx 8$ kg of oxygen, i.e., three times as much. It follows from similar calculations that the combustion of 1 kg of metals and boron requires less oxygen (see Table 13).

Quantitative relations in which the substances react with one another without leaving a residue are called stoichiometric. The stoichiometric relation $\lambda_0 = \frac{\text{kg of oxidizer}}{\text{kg of fuel}}$ is known as the stoichiometric coefficient of a combustible mixture of rocket propellant, whose composition includes both the fuel and the oxidizer.

In jet and piston engines, air is used for the combustion of fuel. Air contains 23.1% oxygen (by weight), i.e., 1 kg of air contains 0.231 kg of oxygen. Hence, the amount of air required (denoted by l_0) is $1/0.231$, i.e., 4.33 times the required amount of oxygen: for hydrogen, 34.4 kg, and for carbon, 11.5 kg [23, 73].

STOICHIOMETRIC COEFFICIENT OF COMPOSITE FUELS

To determine how much oxygen will be required for the complete combustion of 1 kg of composite fuel, it is necessary to know its elemental composition, i.e., its content by weight in the combustible elements $[C]_g$, $[H]_g$, etc., and its oxygen content $[O]_g$ if it is present in the combustible substance. Obviously, the complete combustion of 1 kg of fuel will require the following amount of oxygen (in kg):

$$\lambda_0 = 2.66 [C]_g + 7.94 [H]_g - [O]_g \quad (1.2)$$

Example. The combustion of 1 kg of kerosene, consisting of 0.86 kg of carbon and 0.14 kg of hydrogen, will require $\chi_0 = 0.86 \cdot 2.66 + 0.14 \cdot 7.94 = 3.40$ kg of oxygen or $l_0 = \frac{3.40}{0.231} = 14.7$ kg of air.

Values of the stoichiometric coefficient of various combustibles calculated from formula (1.2) are listed in Table 1.

The more hydrogen is present in a hydrocarbon fuel, the more oxygen is required for the complete combustion of the fuel. In the combustion of alcohol or some other oxygen-containing combustible, a correspondingly smaller amount of oxygen is required from the outside. A small amount of oxygen is also required for combustibles containing nitrogen, since during the combustion of the fuel, nitrogen passes almost completely to the free state, forming N_2 molecules. If the fuel contains boron and metals, the terms $2.22 [B]_g$, $0.89 [A]_g$, etc. are correspondingly added (according to Table 13 to formula (1.2) [9, 55, 73, 81 86].

Table 1. Amount of oxygen and air required for the complete oxidation of certain combustibles (kg of oxidizer/kg of combustible) [23, 73, 86.]

1. Горючее (безводное)	2. Химическая формула	3. Молекулярная масса	4. Элементарный состав в кг/кг			8. Потребное количество кислорода	9. Потребное количество воздуха
			5. углерод $[C]_r$	6. водород $[H]_r$	7. кислород $[O]_r$ и другие элементы		
10. Углеводороды:							
11. Парафиновые	$C_n H_{2n+2}$ ($n = 5 \div 18$)	72—236	0,845	0,155	—	3,49	15,05
12. Нафты, олефины	$C_n H_{2n}$	14,03—	0,857	0,143	—	3,43	14,78
13. Ароматические	$C_n H_{2n-6}$ ($n = 7 \div 10$)	92—134	0,90	0,10	—	3,20	13,8
14. Бензины, керосины	$C_n H_m$	100—200	0,86	0,14	—	3,40	14,7
15. Каучук бутадиевый	$(C_4 H_6 \cdot C_2 H_2 \cdot C_6 H_5)_r$	158,24—	0,912	0,088	—	3,13	13,6
16. Метан	CH_4	16,05	0,749	0,251	—	3,98	17,23
17. Кислородсодержащие горючие:					21. Кислород $[O]_r$		
18. Метиловый спирт	$CH_3 OH$	32,04	0,375	0,125	0,500	1,50	6,47
19. Этиловый спирт	$C_2 H_5 OH$	46,06	0,522	0,130	0,348	2,09	9,00
20. Каучук полисульфидный	$(C_4 H_8 OS_4)_r$	200,37—	0,240	0,040	0,080	0,88	3,81
					22. $[S]_r$ 0,64	1,52	6,58

23. Приблизительные данные.
24. Без сгорания серы.
25. Со сгоранием серы.

1. Горючее (безводное)	2. Химическая формула	3. Молекулярная масса	4. Элементный состав в кг/кг			8. Потребное количество кислорода %	9. Потребное количество воздуха %
			5. углерод [C] _г	6. водород [H] _г	7. кислород [O] _г и другие элементы		
26. Азотсодержащие горючие:					39. Азот [N] _г :		
27. Аммиак	NH ₃	17,03	—	0,176	0,824	1,41	6,07
28. Гидразин	N ₂ H ₄	32,05	—	0,125	0,875	1,00	4,33
29. Метилгидразин	CH ₃ N ₂ H ₃	46,07	0,261	0,131	0,608	1,73	7,43
30. Диметилгидразин	(CH ₃) ₂ N ₂ H ₄	60,09	0,400	0,133	0,467	2,12	9,16
31. Триэтиламин	(C ₂ H ₅) ₃ N	101,18	0,713	0,148	0,139	3,09	13,33
32. Ксилидин	(CH ₃) ₂ C ₆ H ₃ NH ₂	121,23	0,793	0,116	0,091	3,04	13,06
33. Каучук полиуретановый	[NHCOO(CH ₂) ₆] _г	143,18 ^x	0,588	0,091	0,099 [O] _г 0,215	2,08	9,00
34. Нитроцеллюлоза	[C ₇ H ₆ O ₂ (OH) ₁₋₂ (ONO ₂) ₂₋₃] _г	272,4	0,265	0,028	[N] _г 0,126 ¹ [O] _г 0,531 ¹	0,316	1,37
35. Борсодержащие горючие:					40. Бор [B] _г :		
36. Пентаборан	B ₅ H ₉	67,17	—	0,141	0,859	3,03	13,10
37. Декаборан	B ₁₀ H ₁₄	122,31	—	0,114	0,886	2,88	12,45

32. ¹ Приблизительные данные.

Table 1. Amount of oxygen and air required for the complete oxidation of certain combustibles (kg of oxidizer/kg of combustible) [23, 73, 86].
Key:

1. Combustible, anhydrous; 2. Chemical formula; 3. Molecular weight; 4. Elemental composition, kg/kg; 5. Carbon [C]_г; 6. Hydrogen [H]_г; 7. Oxygen [O]_г and other elements; 8. Amount of oxygen required, χ_0 ; 9. Amount of air required, λ_0 ; 10. Hydrocarbons: 11. Paraffins; 12. Naphthenes, olefins; 13. Aromatic; 14. Gasolines, kerosenes; 15. Butadiene-styrene rubber; 16. Methane; 17. Oxygen-containing combustibles; 18. Methanol; 19. Ethanol; 20. Polysulfide rubber; 21. Oxygen [O]_г; 22. [S]_г; 23. ¹Approximate data; 24. ²Without combustion of sulfur; 25. ³With combustion of sulfur; 26. ⁴Nitrogen-containing combustibles; 27. Ammonia; 28. Hydrazine; 29. Methylhydrazine; 30. Dimethylhydrazine; 31. Triethylamine; 32. Xylidine; 33. Polyurethane rubber; 34. Nitrocellulose; 35. Boron-containing combustibles; 36. Pentaborane; 37. Decaborane; 38. ¹Approximate data; 39. Nitrogen; 40. Boron

Excess Oxidizer Coefficient

The actual composition of a fuel mixture in engines usually differs from the stoichiometric composition. It is ordinarily expressed by the coefficient of oxidizer excess (or air excess if air is used as the oxidizer), α , which is the ratio of the actual amount of oxidizer (or air) in the mixture to the stoichiometric amount. When $\alpha = 1$ (stoichiometric mixture), complete combustion of the fuel is achieved with no residue of excess oxidizer. When $\alpha > 1$ (lean mixture), excess oxidizer remains after the complete oxidation of the combustible. When $\alpha < 1$ (rich mixture), because of an insufficient amount of oxidizer, incomplete combustion takes place, and the combustion products contain carbon monoxide CO, sometimes free carbon (soot), hydrogen H_2 , simple hydrocarbons, and other combustible substances [55, 97].

HEAT OF COMBUSTION OF A FUEL

Gross and Net Calorific Value

The heat of combustion (calorific value) is the amount of heat liberated by the complete combustion of 1 kg of fuel and cooling of the combustion products to the initial temperature (usually, 20°C). It is determined experimentally by burning 0.5-0.6 g of fuel in a compressed oxygen medium in a calorimeter (Fig. 2). The heat evolved is calculated from the rise in the temperature of the water in the calorimetric vessel.

The water vapor formed by the combustion of the fuel (oxidation of hydrogen) in the calorimeter condenses, evolving about 600 kcal/kg of water. The calo-

rimetric heat of combustion is known as the gross heat of combustion (H_0).

During the operation of engines, the heat of condensation of the vapor discharged into the atmosphere is not used, and the fuel is therefore characterized by using the net heat of combustion, which is the gross value minus the heat of condensation of water vapor:

$$H_u = H_0 - 600W, \quad (1.3)$$

where W is the amount of water in kg formed by the combustion of 1 kg of fuel.

For standard hydrocarbon fuels, $W = 1.15$ to 1.35 kg of water/kg of fuel. Hence, H_u is smaller than H_0 by approximately 700-800 kcal/kg. The value of W is found from the hydrogen content $[H]$ of the fuel ($W = 9 [H]$ kg of water/kg of fuel) or by direct measurement of the amount of water formed in the calorimeter [27, 73, 97].

Figure 2. Diagram of calorimeter.

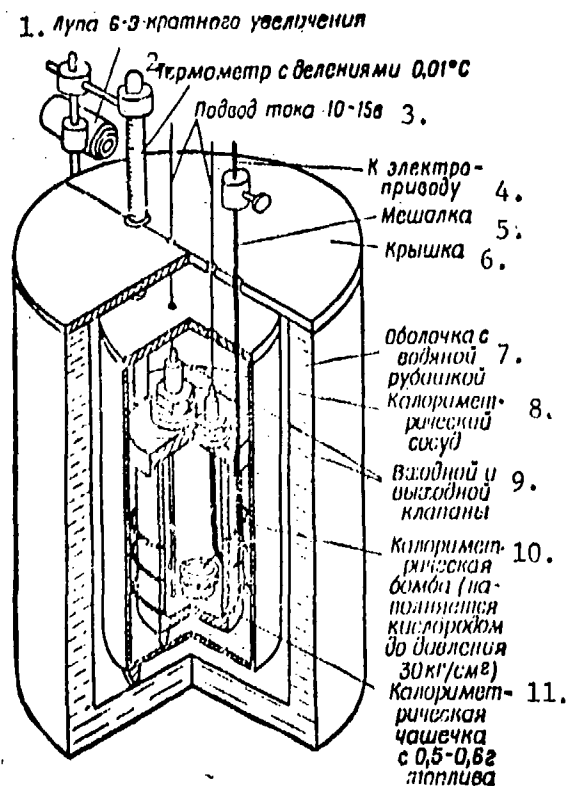


Figure 2. Diagram of calorimeter. Key:

1. 6-9 x magnifying glass;
2. Thermometer with 0.01°C divisions;
3. 10-15 V current supply;
4. To electric drive;
5. Stirrer;
6. Lid;
7. Housing with water jacket;
8. Calorimetric vessel;
9. Entrance and exit valves;
10. Calorimetric bomb (filled with oxygen up to a pressure of 30 kg/cm²);
11. Calorimetric cup with 0.5-0.6 g of fuel.

DEPENDENCE OF THE HEAT OF COMBUSTION OF A FUEL ON ITS CHEMICAL COMPOSITION

The heat of combustion depends on the elemental composition of the fuel and on the strength of the bonds in the molecules of the fuel and oxidation products. The liberation of thermal energy during the combustion may be visualized as the result of two processes (Fig. 3):

1) rupture of the relatively weak chemical bonds C-C, C-H, and others between atoms in the combustible and oxidizer molecules, energy being consumed in this process (the energy supplied is assigned a plus sign¹);

2) formation of strong chemical bonds between the atoms of the combustible and oxidizer elements, H-O, C-O and others, in the oxide molecules, this process involving the liberation of energy (since the process is considered at constant temperature, this energy is removable, and is assigned a minus sign). Each chemical bond has a certain bond energy: the C-C bond, 85-90 kcal/mole; the C=C bond, 145 kcal/mole; the C-H bond, 95-98 kcal/mole; the H-H bond, 103 kcal/mole; the O-O bond, 118 kcal/mole; the H-O bond, 115 kcal/mole; the C-O bond, 150 kcal/mole, etc. Thus, the chemical energy of substances is expressed in thermal units [39, 73, 86]

¹This sign rule, opposite to the one used in chemistry, is usually employed in thermodynamic calculations and handbooks.

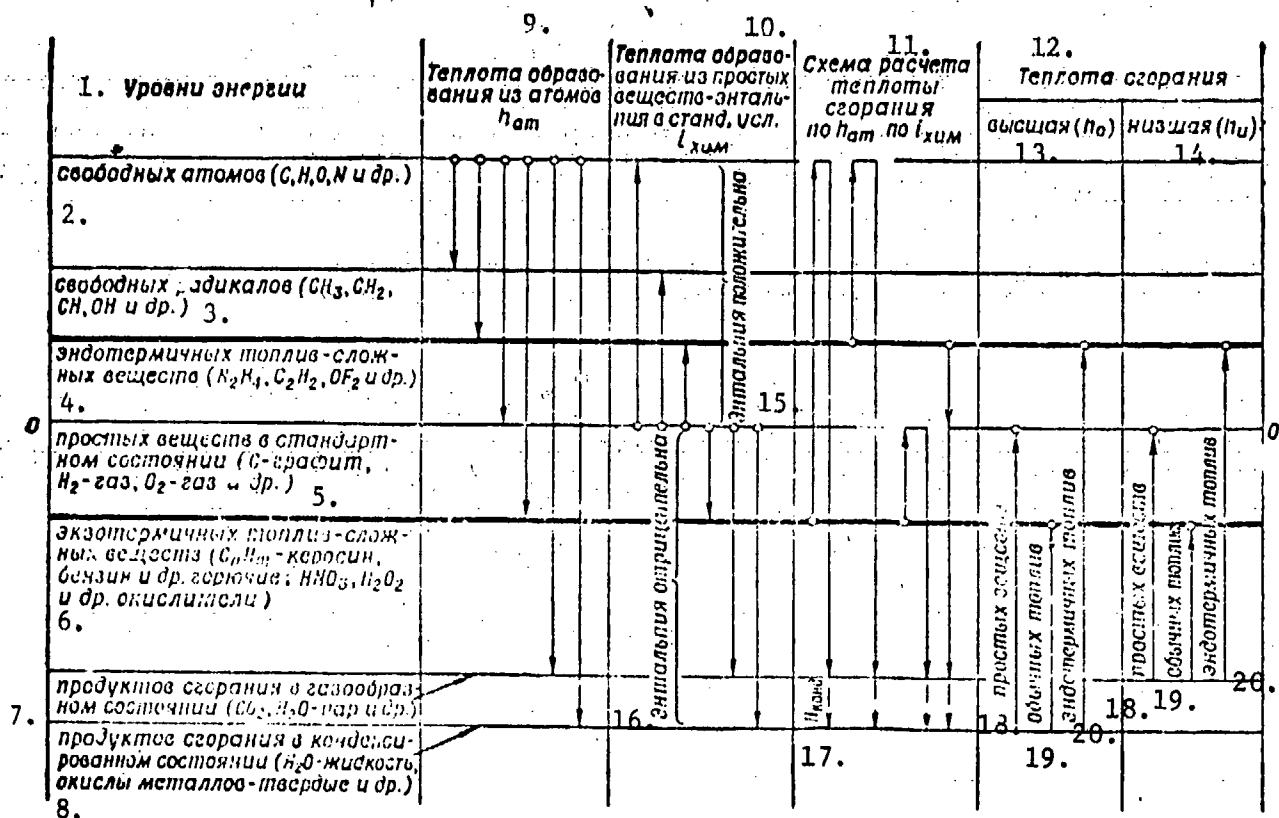


Fig. 3. Diagram of the relationship between the heat of formation, enthalpy, and calorific value of a fuel (for a conventionally isothermal combustion process, the liberated heat is removable and has a minus sign). Key:

Energy levels; 2. of free atoms (C, H, O, N, etc.); 3. of free radicals (CH_3, CH_2, CH, OH , etc.); 4. Endothermic fuels - compounds (N_2H_4, C_2H_2, OF_2 , etc.); 5. Elements in the standard state (C-graphite, H_2 -gas, O_2 -gas, etc.); 6. Exothermic fuels - compounds (C_nH_m - kerosene, gasoline, and other combustibles; HNO_3, H_2O_2 , and other oxidizers); 7. Combustion products in the gaseous state (CO_2, H_2O - vapor, etc.); 8. Combustion products in the condensed state (H_2O - liquid, metal oxides - solids, etc.); 9. Heat of formation from the atoms $h_{ат}$; 10. Heat of formation from the elements - enthalpy at standard conditions, $i_{хим}$; 11. Scheme for calculating the heat of combustion from $h_{ат}$ and from $i_{хим}$; 12. Heat of combustion; 13. Gross (h_0); 14. net h_u ; 15. Positive enthalpy; 16. Negative enthalpy; 17. H_{cond} ; 18. of elements; 19. of standard fuels; 20. of endothermic fuels.

Total Enthalpy

In thermodynamics, use is made of the concept of enthalpy $i = u + RT = C_p T$ (where u is the internal energy. C_p is the heat capacity at constant pressure, R is the gas constant, and T is the absolute temperature). Its change takes place whenever energy is supplied or removed. When the fuel passes from one state to another (for example, when gases are liquefied or in allotropic transformations) and during dissociation of combustion products, it is the most convenient way of expressing energy changes. By convention, the total enthalpy of elements at standard temperature 20°C in the ordinary stable state (the gases H_2 , C_2 , solid graphite C , etc.) is assumed to be equal to zero. The enthalpy of a compound at standard conditions is therefore equal to the heat of formation of the compound from the elements. For combustibles, it is usually low; for example, for the mixture of hydrocarbons forming petroleum fuel, $i = -400$ to -500 kcal/kg. Much more heat is liberated by the formation of oxides: for CO_2 , $i = 2140$ kcal/kg, and for H_2O , $i = -3210$ kcal/kg (at 20°C). The calorific value of a combustible is equal to the difference between the enthalpy of the combustible and that of its combustion products (oxides) [55, 77].

$$H_u = i_g - i_{cp} \quad (1.4)$$

Calculation of Calorific Value

Figure 3 (right) shows that the calorific value as the thermal effect of decomposition of a compound into atoms and formation of oxides from the atoms is the same as the thermal effect of decomposition of a compound into elements and oxidation of the elements.

1. Наименование горючего элемента и состояние простого вещества	2. Окисление газообразным кислородом (O ₂)		3. Окисление газообразным фтором (F ₂)	
	4. Продукт сгорания и его состояние	5. Теплотворность	4. Продукт сгорания и его состояние	5. Теплотворность
6. Углерод (C) твердый (графит)	CO ₂ , газ; 13. CO, газ; 14.	7850; 2200	CF ₄ , газ 31.	18 340
7. Водород (H ₂), газ	H ₂ O, пар 15.	27. Низшая 28 700	HF, газ 31.	64 300
8. Бор (B) твердый	B ₂ O ₃ , твердый (ниже 450° C), 17. B ₂ O ₃ , жидкий (выше 450° C), 18. B ₂ O ₃ , газ (выше 2225° C)	27. 14 000, 2-я высшая 13 760, 27. Низшая 9200	BF ₃ , газ 31.	25 000
9. Магний (Mg) твердый	MgO, твердый (ниже 2800° C), 20. MgO, газ (выше 3600° C)	30. Высшая 5930, 27. Низшая -170	32. MgF ₂ , твердый, 33. MgF ₂ (выше 1263° C)	Высшая 10 700, Низшая 7200
10. Алюминий (Al) твердый	Al ₂ O ₃ , твердый (ниже 2050° C), 21. Al ₂ O ₃ , газ (выше 2700° C)	30. Высшая 7400, 27. Низшая 4130	34. AlF ₃ , твердый (ниже 1040° C), 35. AlF ₃ , газ (выше 1280° C)	Высшая 13 200; Низшая 10 600
11. Бериллий (Be) твердый	BeO, твердый (ниже 2550° C), 23. BeO, газ (выше 3900° C)	30. Высшая 15 900, 27. Низшая -3100	36. BeF ₂ , твердый (ниже 540° C), 37. BeF ₂ , газ (выше 1170° C)	Высшая 26 800; Низшая 20 800
12. Литий (Li) твердый	Li ₂ O, твердый, 25. (ниже 1430° C), 26. Li ₂ O, газ (выше 1700° C)	30. Высшая 10 300, 27. Низшая 2880	38. LiF, твердый (ниже 850° C), 39. LiF, газ (выше 1690° C)	Высшая 21 100; Низшая 11 450

Table 2. Calorific value of major combustible elements, kcal/kg of combustible [86]. Key:

1. Element and its state; 2. Oxidation by gaseous oxygen (O₂);
3. Oxidation by gaseous fluorine (F₂); 4. Combustion product and its state; 5. Calorific value; 6. Carbon (C), solid (graphite);
7. Hydrogen (H₂), gas; 8. Boron (B), solid; 9. Magnesium (Mg),
10. Aluminum (Al), solid; 11. Beryllium (Be), solid; 12. Lithium (Li), solid; 13. CO₂, gas; 14. CO, gas; 15. H₂O, vapor;
16. B₂O₃, solid (below 450°C); 17. B₂O₃, liquid (above 450°C);
18. B₂O₃, gas (above 2225°C); 19. MgO, solid (below 2800°C);
20. MgO, gas (above 3600°C); 21. Al₂O₃, solid (below 2050°C);
22. Al₂O₃, gas (above 2700°C); 23. BeO, solid (below 2550°C)
24. BeO, gas (above 3900°C); 25. Li₂O, solid (below 1430°C);
26. Li₂O, gas (above 1700°C); 27. Net; 28. First gross;
29. Second gross; 30. Gross; 31. Gas; 32. MgF₂ solid;
33. MgF₂ (above 1263°C); 34. AlF₃, solid (below 1040°C)
34. AlF₃, solid (below 1040°C); 35. AlF₃, gas (above 1280°C)
36. BeF₂, solid (below 540°C); 37. BeF₂, gas (above 1170°C);
38. LiF, solid (below 850°C); 39. LiF, gas (above 690°C)

The calorific value of the most important combustible elements during oxidation by oxygen and fluorine is shown in Table 2; it is equal to the enthalpy of the corresponding oxidation products with the sign reversed, referred to 1 kg of combustible. During combustion in fluorine, more heat is liberated than in oxygen (in terms of 1 kg of combustible). The liberation of heat during the combustion of metals depends on the composition of the products of their oxidation (solid, liquid, or gaseous). Accordingly, the gross and net calorific values are distinguished for metals; the net value does not include the heat of condensation of the oxidation product of the metal. The combustion of metals may be of interest when chiefly solid combustion products are formed, but not gaseous ones. The formation of gaseous oxides of magnesium (Mg) and beryllium (Be) consumes even more heat than their combustion evolves [9].

Calorific Value of Compounds

The complete oxidation of 1 kg of pure carbon (graphite) by gaseous molecular oxygen O_2 liberates 7850 kcal, and that of 1 kg of molecular hydrogen H_2 to water vapor, 28,700 kcal (3.66 times as much). On the basis of expression (1.4), the heat of combustion of kerosene, gasoline, or other substance whose combustible elements are carbon and hydrogen, during combustion of gaseous oxygen or in air, may be determined from its elemental composition and the total enthalpy i_g known from handbooks (equal at $20^\circ C$ to the heat of formation from the elements):

$$H_e = 7850 [C]_g + 28,700 [H]_g + i_g, \quad (1.5)$$

where $[C]_g$ and $[H]_g$ are the contents of carbon and hydrogen in 1 kg of combustible [kg/kg].

Instead of adding the enthalpy or heat of formation, one can subtract the heat of decomposition Q_{dec} into the elements ($Q_{dec} = -l_g$).

Example. The calorific value of kerosene, 1 kg of which contains 0.86 kg of carbon and 0.14 kg of hydrogen, and the total enthalpy $l_g = -450$ kcal/kg according to (1.5) will be $H_e = 7850 \cdot 0.86 + 28,700 \cdot 0.14 - 450 = 10,350$ kcal/kg.

The more hydrogen is present in a fuel, the higher its heat of combustion. Thus, paraffin hydrocarbons C_nH_{2n+2} , which contain 1.5-2 times as much hydrogen as aromatic ones, have a much higher calorific value. If the fuel contains boron and metals, one adds $14,000 [B]_g$, $7400[Al]_g$, etc., to formula (1.5) (the weight fraction of each element is multiplied by its calorific value). If the oxidizer is fluorine, then into an expression analogous of formula (1.5), one substitutes values of the calorific value of the combustible elements for the reaction with fluorine, listed in Table 2. Heats of combustion of certain hydrocarbons, hydrocarbon fuels, and combustible components of rocket fuel, calculated from formula (1.5), are given in Table 3 [16, 27, 55, 73, 81, 86].

Endothermic Compounds

There are compounds whose formation from the atoms involves the liberation (removal) of less heat than the amount consumed (supplied) in decomposing the molecules of the elements into atoms. Hence, the formation of this type of compounds from the elements is not associated with the liberation of heat, as in the usual case, but with the absorption of heat; they are therefore called

endothermic. The total enthalpy of such compounds at standard conditions according to the adopted sign rule is positive (see Table 3), and the calorific value is higher than the total heat of combustion of the number of combustible elements contained therein (Fig. 3) [16, 39, 73].

Other Energy Effects

For cryogenic¹ fuels (liquefied gases) such as liquid ammonia and liquid hydrogen, the total enthalpy and heat of combustion are calculated, not for 20°C, but the boiling point. Determination of total enthalpy for a nonstandard temperature consists in adding to the standard enthalpy (heat of formation) the energy effects of cooling of the gaseous substance from 20°C to the boiling point.

$$q = C_{ptb} - C_p \cdot 20$$

(for ammonia, this value is -25 kcal/kg, and for hydrogen, -860 kcal/kg), condensation to the liquid (for ammonia, -327 kcal/kg; for hydrogen, -108 kcal/kg), and other changes of state of the substance if they occur in the course of cooling. In particular, the equilibrium state of gaseous hydrogen at 20°C corresponds to a 75% content of ortho hydrogen (the protons of the five atoms in the H₂ molecule have parallel spins and 25% para hydrogen (the protons of the two atoms in the H₂ molecule have opposite spins), while at the boiling point, nearly pure (99.8%) para hydrogen is the equilibrium form. The total heat of the ortho-para transition is -168 kcal/kg, and for 0.75 kg of hydrogen participating in this transition, it is 0.75 (-168) = -126 kcal/kg.

The temperature of combustion of mixtures consisting of components not bound chemically to one another may be calculated from the formula

$$H_{mix} = aH_a + bH_b + cH_c + \dots + Q_{so} \quad (1.6)$$

¹The term cryogenic is composed of the Greek words kryos - cold, and genos - birth, i.e., literally means "generated by the cold."

Table 3. Heat of combustion and certain physical properties of fuels and combustible components of rocket fuel [86]. Key:

1 Топлива и горючие компоненты	2. Полная энтальпия при 20° С, ккал/кг	3 Теплота сгорания (расчетная), ккал		6. Плотность при 20° С, кг/л	7 Температура, °С	
		кг горючего			8. кипения	9. замерзания
		4 окисление кислородом (O ₂)	5. окисление фтором (F ₂)			
10. Углеводороды.						
11. Парафиновые (C _n H _{2n+2} ; n = 5÷18)	—500 ²	10500 ²	25000 ²	0,66—0,75	36—220	—130÷+18
12. Нафты, олефины (C _n H _{2n} ; n = 5÷18)	—400 ²	10400 ²	21500 ²	0,74—0,80	50—220 ²	—93÷+6
13. Ароматические (C _n H _{2n-6} ; n = 7÷10)	—150 ²	9800 ²	22800 ²	0,86—0,88	100—200	—95÷+13
14. Бензины, керосины (C _n H _m)	420÷460 ²	10350 ²	24300 ²	0,72—0,85	40—300	—60 ²
15. Каучук бугадиенсти- рольный (C ₁₂ H ₁₄) _x	+520 ²	10200 ²	22900 ²	—	—	—
16. Метан (CH ₄) жидкий (при —162° С)	—1260 ²	11820 ²	27600 ²	0,424 ²	—162	—182
17. Кислородсодержащие горючие:						
18. Метиловый спирт (CH ₃ OH)	—1780	4750	13100	0,791	65	—98
19. Этиловый спирт (C ₂ H ₅ OH)	—1450	6380	16500	0,789	78	—114
20. Каучук полисульфид- ный (C ₈ H ₈ OS ₂) _x	+1000 ²	5600 ²	8000 ²	—	—	—
21. Азотсодержащие горючие и составные части твердого топлива:						
22. Аммиак (NH ₃) жидкий (при —33° С)	—990 ¹	4060	10300	0,682 ²	—33	—78
23. Гидразин (N ₂ H ₄)	+380	3970	8420	1,008	144	+2
24. Метилгидразин (CH ₃ N ₂ H ₃)	+280	6090	13500	0,876	8 ²	—52
25. Диметилгидразин (CH ₃) ₂ N ₂ H ₂	+190	7140	16100	0,792	63	—57
26. Триэтилмин (C ₂ H ₅) ₃ N	—395	9460	22200	0,729	90	—114
27. Ксилантин (CH ₃) ₂ C ₆ H ₃ NH ₂	—380	9160	21600	0,978	212	—54

28. ¹ Молекулярная масса и элементный состав приведены в табл. 1.

29. ² Приблизительные данные.

30. ² При температуре кипения.

(Table 3 continued following page)

1. Топлива и горючие компоненты	2. Полная энтальпия при 20° С, ккал./кг	3. Теплота сгорания (расчетная), ккал. на горючего		6. Плотность при 20° С, кг/л	7. Температура, °С	
		окисление кислородом (O ₂)	окисление фтором (F ₂)		8. кипения	9. замерзания
33. Каучук полиуретановый [NHCOO (CH ₂) ₆] _x	+50	7250	16 700	—	—	—
34. Нитроцеллюлоза [C ₆ H ₇ O ₂ (OH)] _x (ONO ₂) ₂₋₃	-590	1025	—	1,66	—	—
35. Нитроглицерин C ₃ H ₅ (ONO ₂) ₃	-400	1490	—	1,58	—	+13,2
36. Борсодержащие горючие:						
37. Пентаборан (B ₅ H ₉)	+150	16 000	30 700	0,63	62	-47
38. Декаборан (B ₁₀ H ₁₄)	-170	15 400	29 700	0,92	219	+99
39. Водород жидкий (H ₂ при -253° С)						
40. Нормальный водород (0,75 орто + 0,25 пара)	-950	27 750	63 300	0,071	-263	-259
41. Параводород	-1200	27 500	63 100	—	—	—

30. При температуре кипения.

31. Без потребления извне.

32. При образовании борного ангидрида в жидком виде.

Table 3. Heat of combustion and certain physical properties of fuels and combustible components of rocket fuel [86] Key:

1. Fuels and combustible components; 2. Total enthalpy 20°C, kcal/kg; 3. Heat of combustion, (calculated), kcal/kg of combustible; 4. Oxidation by oxygen (O₂); 5. Oxidation by fluorine (F₂); 6. Density at 20°C, kg/ ; 7. Temperature, °C; 8. Boiling; 9. Freezing; 10. Hydrocarbons: 11. Paraffin (C_nH_{2n+2}; n = 5 to 18); 12. Naphthenes, olefins (C_nH_{2n}; n = 5 to 18); 13. Aromatic (C_nH_{2n-6}; n = 7 to 10); 14. Gasolines, kerosenes (C_nH_m); 15. Butadiene-styrene rubber (C₁₂H₁₄)_x; 16. Methane (CH₄), liquid (at -162°C); 17. Oxygen-containing combustibles: 18. Methanol (CH₃OH); 19. Ethanol (C₂H₅OH); 20. Polysulfide rubber (C₄H₈OS₄)_x; 21. Nitrogen-containing combustibles and ingredients of solid fuel: 22. Ammonia (NH₃), liquid (at -33°C); 23. Hydrazine (N₂H₄); 24. Methylhydrazine (CH₃N₂H₃); 25. Dimethylhydrazine (CH₃)₂N₂H₂; 26. Triethylamine (C₂H₅)₃N; 27. Xylidine (CH₃)₂C₆H₃NH₂; 28. 1The molecular weight and elemental composition are given in Table 1; 2Approximate data; 3At the boiling point. 31. 4Without consumption from outside; 32. 5Boric anhydride being formed in the liquid state; 33. Polyurethane rubber; 34. Nitrocellulose; 35. Nitroglycerin; 36. Boron-containing combustibles; 37. Pentaborane (B₅H₉); 38. Decaborane (B₁₀H₁₄); 39. Liquid hydrogen (H₂ at -253°C); 40. Normal hydrogen (0.75 ortho + 0.25 para); 41. Parahydrogen.

where a, b, c are the fractions of the components in the mixture (kg/kg of fuel);

H_a, H_b, H_c are the calorific values of the component;

Q_{sol} is the heat of solution for real fuels, it is usually negligibly low).

The water present in certain fuels consumes about 600 kcal/kg on vaporization. Hence, its calculated "calorific value" is expressed by the number -600 kcal/kg. The total enthalpy at 20°C for water vapor is -3210 kcal/kg, and for liquid water, 600 kcal/kg less, i.e., approximately -3800 kcal/kg [9, 39, 67].

Calorific Value of a Combustible Mixture

The heat of combustion in terms of 1 kg of combustible mixture (or 1 kg of rocket fuel containing the combustible and oxidant) is determined from the calorific value of the combustible, oxidizer and their ratio. In the simplest case, when the oxidizer is air, and the calorific effect of the oxidizer is equal to zero, the calorific value of the mixture at a coefficient of excess oxidizer $\alpha \geq 1$ (i.e., when the combustible is completely oxidized) is expressed by the formula

$$h_a = \frac{H_u}{1 + \alpha l_0} \quad (1.7)$$

With increasing excess of air, the amount of heat transferred to 1 kg of the combustion products decreases (Fig. 4, region of lean mixtures). In the region of rich mixtures, the combustible is not completely oxidized, the liberation of heat $H_\alpha < H_u$, and, despite the decrease in the amount of oxidizer αl_0 , the liberation of heat h_α in terms of 1 kg of combustion products also decreases.

The specific law of change of h_u in the region of rich mixtures depends on the fuel composition. Because of the low evolution of heat, the flame cannot propagate in a very rich or very lean mixture [1, 97].

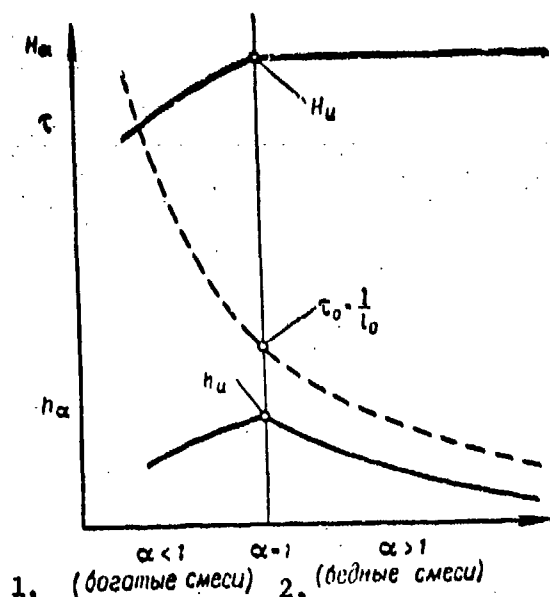


Fig. 4. Effect of composition of combustible H_u and fuel h_u (dashes indicate the change of the combustible fraction in the

mixture $\gamma = \frac{G_g}{G_a}$. Key:

1. (rich mixtures); 2. (lean mixtures).

FUEL AS A SOURCE OF WORKING SUBSTANCE

Role of the Working Substance

Gaseous combustion products serve as the working substance by means of which heat energy is converted into chemical energy in the engine. The formation of a large volume of gases (in the absence of condensed combustion products) promotes a higher speed of their discharge from the engine nozzle, and hence, a higher thrust. For the same calorific value, fuels whose combustion products have lower temperatures are more suitable. This decreases the partial decomposition of the combustion products (dissociation), which absorbs heat and lowers

the economy of the engine, and also reduces the danger of damage to materials of the hot part of the engine [55, 72, 100].

Gas Formation

By gas formation is meant the volume of gases formed by the combustion of 1 kg of fuel (V_{gas}), reduced to standard conditions (760 Torr, 0°C). It can be calculated, knowing that 1 kg-mole of any gas at standard conditions has a volume of 22,415 ℓ and hence, the volume of 1 kg of gas in standard liters (ℓ) reduced to conditions at 760 Torr and 0°C is

$$V_{\text{gas}} = \frac{22.415}{\mu} \quad (1.8)$$

1. Химический элемент	2. Продукт сгорания или газ, содержащийся в продуктах сгорания	3. Моле- куляр- ная масса	Объем в нормальных литрах (760 мм. ст., 0°C)		7. Количе- ство теп- ла, выде- ляемого на 1 кг газа, ккал
			5. 1 кг продуктов сгорания	6. газа, обра- зуемого после сго- рания из 1 кг эле- мента	
8. Углерод (C)	13. Углекислый газ (CO_2)	44,01	509	1865	4,22
	14. Окись углерода ¹ (CO)	28,01	800	1865	1,18
	15. Четырехфтористый углерод (CF_4)	88,01	255	1865	9,82
9. Водород (H)	16. Водяной пар (H_2O)	18,02	1243	11120	2,59
	17. Фтористый водород (HF)	20,01	1119	22230	2,89
	18. Водород ¹ (H_2)	2,02	—	11120	—
10. Азот (N)	19. Азот (N_2)	28,02	—	800	—
11. Кислород (O)	20. Кислород ² (O_2)	32	—	701	—
12. Бор (B)	21. Борный ангидрид (B_2O_3), газ	69,64	322	1035	8,9
	22. Фторид бора (BF_3)	67,82	330	2070	12,0

23.¹ При неполном сгорании топлива (например, при $\alpha < 1$).

24.² При избытке окислителя ($\alpha > 1$).

Table 4. Gas formation during combustion of major combustible elements, standard volume of certain gases, and amount of heat evolved per 1 s ℓ of gases (neglecting dissociation) [9, 81, 100].

Caption for Table 4.

Table 4. Gas formation during combustion of major combustible elements, standard volume of certain gases, and amount of heat evolved per 1 sl of gases (neglecting dissociation) [9, 81, 100]. Key:

1. Chemical element; 2. Combustion product or gas contained in the combustion products; 3. Molecular weight; 4. Volume in standard liters (760 Torr, °C); 5. 1 kg of combustion product; 6. Gas formed after combustion from 1 kg of element; 7. Amount of heat liberated per 1 sl of gas, kcal; 8. Carbon (C); 9. Hydrogen (H); 10. Nitrogen (N); 11. Oxygen (O); 12. Boron (B); 13. Carbon dioxide (CO₂); 14. Carbon monoxide¹ (CO); 15. Carbon tetrafluoride (CF₄); 16. Water vapor (H₂O); 17. Hydrogen fluoride (HF); 18. Hydrogen¹ H₂; 19. Nitrogen (N₂); 20. Oxygen² (O₂); 21. Boric anhydride (B₂O₃), gas; 22. Boron fluoride (BF₃); 23. ¹For incomplete combustion of fuel (for example, when $\alpha < 1$). 24. ²In the presence of excess oxidizer ($\alpha > 1$).

Table 4 gives the standard volume, calculated from formula (1.8), of 1 kg of the principal gases that may be present in the combustion products [14]. The table also lists the volume of gas obtained by burning 1 kg of combustible elements.

It is evident from Table 4 that the combustion of hydrogen forms a much larger volume of gases than the combustion of carbon. High-boiling metals combustion products discharged from an engine will evidently be solid or liquid (gas formation equal to zero). The heat evolved by their formation will be used to heat the gaseous combustion products of other elements.

1. Горючее вещество	2. С кислородом			3. С фтором			7.
	4. Газообразо- вание в н.л. (760 мм рт. ст., °C)			4. Газообразо- вание в н.л. (760 мм рт. ст., °C)			
	5. из 1 кг исходного	6. из 1 кг стехиометрической смеси с кислородом	7. Количество теплоты, выделенное на 1 м ³ газа, ккал	5. из 1 кг исходного	6. из 1 кг стехиометрической смеси со фтором	7. Количество теплоты, выделенное на 1 м ³ газа, ккал	
8. Углеводороды:							
9. Парафиновые (C _n H _{2n+2})	3400	760	3,09	5015	540	4,14	
Нафтены, олефины (C _n H _{2n})	3190	720	3,26	4780	520	4,72	
Ароматические (C _n H _{2n-6})	2790	665	3,51	3900	450	4,82	
Бензины	3160	720	3,28	4720	520	4,06	
Керосины	3160	720	3,16	4720	520	4,03	
Метан (CH ₄) жидкий	4200	843	2,81	7015	592	4,67	
10. Спирты:							
11. Метановый (CH ₃ OH)	2440	980	1,94	2785	610	4,70	
12. Этиловый (C ₂ H ₅ OH)	2660	860	2,40	3370	565	4,90	
13. Азотсодержащие горючие:							
14. Аммиак (NH ₃)	2620	1010	1,50	4580	1050	2,25	
Гидразин (N ₂ H ₄)	2090	1045	1,90	3480	1030	2,42	
Диметилгидразин N ₂ H ₂ (CH ₃) ₂	2610	840	2,73	4090	680	3,94	
Триэтиламин N(C ₂ H ₅) ₃	3090	755	3,06	4740	570	4,48	
Ксилитин C ₆ H ₃ NH ₂ (CH ₃) ₂	2740	680	3,35	4230	515	5,09	
15. Борсодержащие горючие:							
16. Пентаборан (B ₅ H ₉)	2460	830	4,92	4920	865	6,23	
Декаборан (B ₁₀ H ₁₄)	2190	795	5,26	4350	840	6,82	
17. Водород (H ₂) жидкий:							
18. Нормальный водород	11 120	1243	2,49	22 230	1119	2,85	
Параводород	11 120	1243	2,47	22 230	1119	2,83	

19. При образовании борного ангидрида в газообразном состоянии.

Caption for Table 5.

Table 5: Gas formation during combustion of various fuels and amount of heat evolved per 1 sc of gas (neglecting dissociation) [9, 81, 100].

1. Combustible; 2. With oxygen; 3. With fluorine; 4. Gas formation in s (760 Torr, °C); 5. From 1 kg of combustible; 6. From 1 kg of stoichiometric mixture with oxygen; 7. Amount of heat evolved per 1 sc of gas, 8. Hydrocarbons: 9. Paraffins (C_nH_{2n+2}), Naphthenes, olefins (C_nH_{2n}) Aromatic (C_nH_{2n-6}) Gasolines, kerosenes, methane (CH₄), liquid; 10. Alcohols; 11. Methanol (CH₃OH); 12. Ethanol (C₂H₅OH); 13. Nitrogen-containing combustibles: 14. Ammonia (NH₃), Hydrazine (N₂H₄); Dimethylhydrazine N₂H₂(CH₃)₂; Triethylamine N(C₂H₅)₃, Xylidine C₆H₃NH₂(CH₃)₂; 15. Boron-containing combustible: 16. Pentaborane (B₅H₉), Decaborane (B₁₀H₁₄); 17. Hydrogen (H₂), liquid; 18. Normal hydrogen, Para hydrogen; 19. 1 During formation of boric anhydride in the gaseous state.

For composite fuels (Table 5), gas formation is calculated from the component elements. It is of particular great importance for rocket engines since their working substance consists entirely of the propellant combustion products, and in jet engines, of atmospheric nitrogen to the extent of over 70%. It is evident from Tables 4 and 5 that after hydrogen, the largest amount of gas (in terms of 1 kg of mixture) is produced by ammonia and hydrazine, followed by dimethylhydrazine and alcohols [72, 73, 81].

Temperature of Combustion Products

The heat balance equation (enthalpy equation) permits one to estimate the effect of gas formation on the final gas temperature t_g . For example, for 1 kg of fuel and 1 kg of air¹ at $\alpha \approx 1$

$$(1 + \ell) (C_{pg}^g t_g - C_{pg}^0 t_0) = \zeta H_u + \ell (C_{ga}^a t_a - C_{pa}^0 t_0) + C_f^f t_f - C_f^0 t_0, \quad (1.9)$$

where H_u is the calorific value of the fuel;

ζ is the combustion efficiency coefficient (usually, 0.95-0.98);

$t_0 = 20^\circ\text{C}$ is the temperature at which the calorific value of the fuel is determined;

t_a and t_f are the initial temperatures of the air and fuel, $^\circ\text{C}$;

C_{pg} and C_{pa} are the average heat capacities (at constant pressure) of the combustion products and air, and C_f is that of the fuel at the temperature indicated by the superscript (taken from tables).

The composition of the combustion products is determined from the fuel composition.

At $\alpha = 1$ (i.e., $\ell = \ell_0$), initial temperature $t_a = t_g = 20^\circ\text{C}$ and $\ell = 1$, from expression (1.9), the temperature t_g is determined as follows:

$$t_g = \frac{H_u}{C_{p_g}^g (1 + \ell_0)} + \frac{C_{p_g}^0}{C_{p_g}^g (1 + \ell_0)} \approx \frac{H_u}{C_{p_g}^g (1 + \ell_0)} \quad (1.9^1)$$

(since the second term amounts to approximately 1% of the value of t_g). The denominator is expressed fairly simple in terms of the gas volume $v_g^{\text{comb}} = \frac{22,415}{22,415} (1 + \ell_0)$, obtained by oxidizing 1 kg of combustible, and the heat capacity of 1 st of gas $C_p^{\text{st}} = \frac{C_{p_m}}{22,415}$ (where C_{p_m} is the molar heat capacity):

$$C_{p_g}^g (1 + \ell_0) = \frac{C_{p_m}}{22,415} (1 + \ell_0) = \frac{C_{p_m}}{22,415} \cdot \frac{22,415}{22,415} (1 + \ell_0) = C_p^{\text{st}} v_g^{\text{comb}}.$$

It follows that

$$t_g \approx \frac{H_u}{C_p^{\text{st}} v_g^{\text{comb}}}.$$

The difference in gas formation for the combustion of fuel of different compositions is more pronounced than the difference in calorific value of the fuel and volume heat capacity, which is slight for different gases. For this reason, the influence of gas formation on the temperature of combustion products frequently proves decisive. The more gas is formed, the less heat will be received by each standard liter of gas, and the lower will be the gas temperature. Thus, owing to a greater gas formation, fuels containing more hydrogen give a lower combustion temperature, and this has a beneficial effect on engine operation. Therefore, for example, paraffinic hydrocarbons ($C_n H_{2n+2}$) have a lower combustion temperature (50-100°C and lower) than aromatic ones

¹The heat balance may be similarly drawn up for any oxidizers and combustibles.

(C_nH_{2n-6}). This is particularly important in increasing the calorific value of a fuel, since it makes it possible to obtain an increase of useful work (specific thrust) directly by increasing the volume (gas constant) of the working substance and not by raising the gas temperature, as this causes a decrease of the efficiency, owing to dissociation of the combustion products [73, 77].

Thermal Dissociation

At high temperatures (above 1800-2000°C), chemical processes involving absorption of heat take place in the gaseous combustion products. They include a partial decomposition (dissociation) of the oxides CO_2 and H_2O into the elements, radicals, and atoms, as well as endothermic exchange reactions.

<u>Reaction</u>	<u>Heat consumed, kcal/kg</u>
$CO_2 \rightarrow CO + 0.5O_2$	1540
$CO \rightarrow C + 0.5O_2$	1060
$H_2O \rightarrow H_2 + 0.5O_2$	3220
$H_2O \rightarrow OH + 0.5H_2$	570
$O_2 \rightarrow O + O$	3640
$H_2 \rightarrow H + H$	6050
$N_2 \rightarrow N + N$	51,300
$N_2 + O_2 \rightarrow 2NO \rightarrow$	360
$CO + H_2O \rightarrow CO_2 + H_2$	220

The higher the temperature of the combustion products, the greater the heat loss due to dissociation and to exchange reactions. The reduction of thermal effect of fuel combustion due to dissociation may be very significant, particularly at low pressures (tenths of percent). Considerable gas formation, which causes a lower temperature of the gases, decreases dissociation and permits a better utilization of the thermal energy of the fuel (Fig. 5). At the same temperature, the dissociation of diatomic molecules (CO , HF , N_2 , etc.) is slight, whereas that of triatomic ones (CO_2 , H_2O) and particularly polyatomic ones (for example, CF_4 , B_2O_3) is more extensive.

Calorific value alone may give a false idea of the efficiency of a fuel. Thus, nitrogen-containing rocket fuel, for example, hydrazine and dimethylhydrazine, which have a moderate calorific value because of low-molecular (small μ) and low-atomic (small number of atoms in the molecule) combustion products, when combining with the same oxidizer, yield a higher specific thrust than combustibles with a higher calorific value (for example, kerosene) forming high-molecular gases (see Table 10).

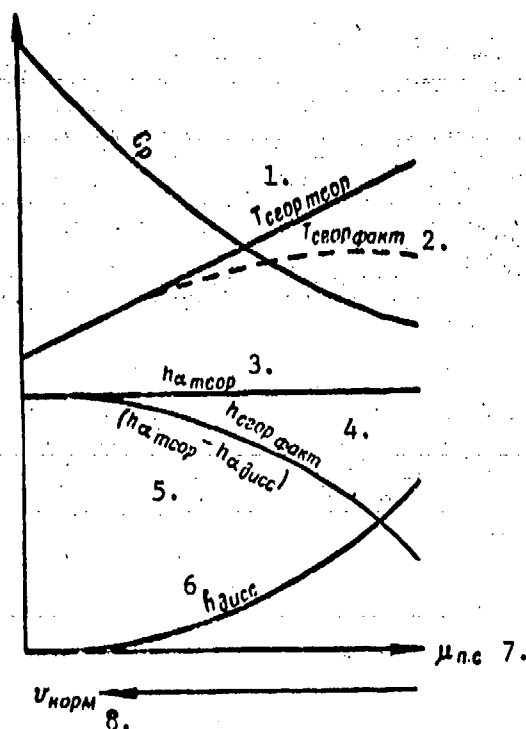


Figure 5. Diagram of the effect of the molecular weight of combustion products on their temperature, on heat loss due to dissociation, and on heat evolved in the combustion chamber. Key:

1. $T_{comb theor}$; 2. $T_{comb акт}$;
3. $h_a theor$; 4. $h_{comb акт}$; 5. $h_a theor - h_a diss$;
6. h_{diss} ; 7. μ_{cp} ; 8. v_{stern} .

Thus, calorific characterizes the available fuel energy, and the thermodynamic properties of the combustion products determine the possibility of its utilization in the production of mechanical work and generation of thrust [9, 55, 36].

FUEL AS A SOURCE OF THRUST IMPULSE

Unit Impulse

By burning fuel, the aircraft engine generates an impulse of thrust which in the course of flight is balanced by the impulses of the gravitational field and drag and by the change the momentum of the aircraft. The feasibility of carrying out a given flight program depends on the impulse required by the liftoff, acceleration, turns, horizontal flight, and on the available thrust impulse, which is determined by the on-board reserve of fuel G_f and the thrust

efficiency of each kilogram of fuel. By consuming 1 kg of the weight of the fuel, the engine generates a unit impulse

$$I_f = \frac{P \tau_1}{G_f} [\text{sec}]$$

where P is the thrust force;

τ_1 is the time of its action during the consumption of 1 kg of fuel.

The unit impulse is equal to the thrust of the engine divided by the fuel-mass flow $\frac{dG_f}{d\tau}$:

$$I_f = \frac{P}{\frac{dG_f}{d\tau}} \left[\frac{\text{kg}}{\text{kg/sec}} \right]. \quad (1.10)$$

The unit impulse has the dimension of time and physically constitutes the time in seconds during which 1 kg of fuel produces 1 kg of engine thrust, or the time during which an amount of fuel numerically equal to the thrust forces is consumed. The larger I_f , the longer the available time $\tau_{av} = I_f \frac{G_f}{P}$ of the work of an engine with thrust P for a given reserve G_f of fuel.

$$I_f = \frac{1}{G_f \text{ sec} / P} = \frac{1}{C_{sp} \text{ sec}} = \frac{3600}{C_{sp} \text{ hr}} \quad (1.11)$$

The quantity C_{sp} is inversely proportional to the calorific value of the fuel, and hence, $I_f \sim H_u$. Thus, the unit impulse of fuel is the thrust equivalent of its energy properties for the operation of any engine in flight [38, 55].

Available Fuel Impulse

As the fuel is consumed, the flying weight decreases. During a time element d , the decrease in weight is $dG = dG_f$, and the unit impulse of the thrust force, referred to a unit of instantaneous weight of the aircraft, is

$$dI_f = \frac{Pd\tau}{G} = \frac{I_f dG_f}{G} = - I_f \cdot \frac{dG}{G}$$

The total impulse imparted to a unit of variable aircraft weight in the total time τ of operation of the engine in flight, during which the flying weight of the aircraft decreases from the initial G_i to the final $G_{fi} = G_i - G_f$, is

$$I_f = - \int_{G_i}^{G_{fi}} \rho_f \frac{dG}{G} = \rho_f \ln \frac{G_i}{G_{fi}} = \rho_f \ln T. \quad (1.12)$$

where $T = \frac{G_i}{G_{fi}}$ is Tsiolkovskiy's number.

V.S. Pyshnov refers to the quantity I_f as the available fuel impulse. Formula (1.12) is an application of the well-known Tsiolkivskiy formula, which he derived for the purpose of determining the maximum velocity of a rocket, to the determination of the characteristics of any flying vehicle [76].

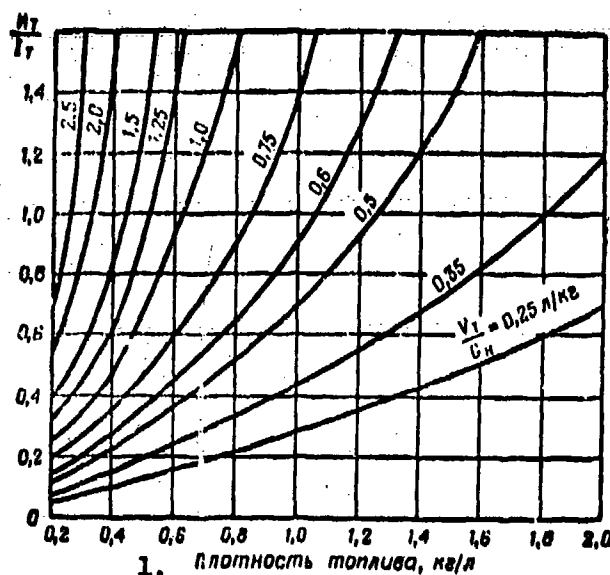
Effect of Fuel Density

The number T and hence, the available fuel impulse depend in certain cases on the fuel density ρ_f . When the fuel tanks are completely filled (V_f), as the density of the fuel ρ_f rises, its weight $G_f = V_f \rho_f$ increases correspondingly.

If the initial flying weight G_1 is given, the number T and the available fuel impulse increase at the cost of a reduction in payload $G_p = G_1 - G_0 - V_f \rho_f$ (G_0 being the weight of the structure, crew, and equipment):

$$T = \frac{G_1}{G_1 - V_f \rho_f} = \frac{1}{1 - \frac{V_f}{G_1} \rho_f} \quad (1.13)$$

$$I_f = \ell_f \ln \frac{1}{1 - \frac{V_f}{G_1} \rho_f}$$



$$\frac{V_f}{G_1} = 0.25 \text{ л/кг}$$

Fig. 6. Effect of fuel density on the thrust impulse imparted to a unit weight of a flying vehicle for the same initial flying weight and specific engine thrust ($\frac{V_f}{G_1}$ being the capacity of the fuel tanks per unit of initial flying weight) Key:

1. Fuel density, kg/l

This is due to the fact that as the weight of the fuel increases, the final weight of the aircraft and the thrust required at the end of the flight

decrease. There is a corresponding decrease in the fuel consumption per kilometer, which increases the flight range. For the same thrust, the velocity or flight altitude will increase, etc.

The effective density turns out to be less pronounced if the problem is to fly with the same payload, and the initial flying weight $G_i = G_0 + G_p + V_f \rho_f$ depends on the reserve of fuel:

$$T = \frac{G_0 + G_p + V_f \rho_f}{G_0 + G_p} = 1 + \frac{V_f}{G_0 + G_p} \rho_f; \quad (1.14)$$

$$I_f = I_f \ln \left(1 + \frac{V_f}{G_0 + G_p} \right) \rho_f.$$

In the case of the same fuel weight ($G_f = \text{const}$), the fuel density does not of course have any effect on the available impulse or the flight capabilities of the aircraft [55, 73].

BASIC INDICES OF PHYSICAL PROPERTIES OF LIQUID FUELS

The quality of a fuel is determined not only by its energy characteristics, but also by such physical properties as density, viscosity, vaporizability, freezing, and also such chemical properties as stability, corrosiveness, etc. For kerosenes and gasolines, whose energy characteristics are almost the same, the physicochemical properties play a decisive role in the determination of capability and of the conditions of use. Standards for the indices of physicochemical properties of each fuel are established by GOST (All-Union State Standard) or by technical specifications.

Density

Density is the mass of a substance contained in a unit of its volume. Since the mass of 1 l of water at 4°C is exactly equal to 1 kg, the numerical value of density expressed in kg/l (g/ml) is equal to the ratio of the mass (or weight) of any volume of a substance to the mass (or weight) of the same volume of water at 4°C. In practice, the dimensionless value of this ratio is taken as the density of fuels, oils, and technical fluids. It is denoted by ρ_t^4 (where t is the temperature of the product at which its density is determined, and 4 is the temperature of water in °C, relative to which the density is expressed). It is numerically equal to the specific gravity of the fuel in the technical unit system. By considering density as a weight quantity, one finds the weight of the fuel $G_f = V_t \rho_t^4$ from the volume V_t and density ρ_t^4 (measured at the same temperature t).

As the temperature rises, the density of fuels decreases, and as it is lowered, the density increases. When the temperature changes by Δt , the density change $\Delta \rho = -\gamma \Delta t$, where γ is the temperature correction for the density of a given substance for 1°C. For petroleum products, $\gamma \approx 0.0005 - 0.0009$ (Table 6).

1. Плотность	2. Поправка	1. Плотность	2. Поправка
0,6900—0,6999	0,000910	0,8500—0,8599	0,000699
0,7000—0,7099	0,000897	0,8600—0,8699	0,000686
0,7100—0,7199	0,000884	0,8700—0,8799	0,000673
0,7200—0,7299	0,000870	0,8800—0,8899	0,000660
0,7300—0,7399	0,000857	0,8900—0,8999	0,000647
0,7400—0,7499	0,000844	0,9000—0,9099	0,000633
0,7500—0,7599	0,000831	0,9100—0,9199	0,000620
0,7600—0,7699	0,000818	0,9200—0,9299	0,000607
0,7700—0,7799	0,000805	0,9300—0,9399	0,000594
0,7800—0,7899	0,000792	0,9400—0,9499	0,000581
0,7900—0,7999	0,000778	0,9500—0,9599	0,000567
0,8000—0,8099	0,000765	0,9600—0,9699	0,000554
0,8100—0,8199	0,000752	0,9700—0,9799	0,000541
0,8200—0,8299	0,000738	0,9800—0,9899	0,000528
0,8300—0,8399	0,000725	0,9900—1,0000	0,000515
0,8400—0,8499	0,000712		

Table 6. Average temperature corrections for the density of petroleum products for 1°C (γ) Key:
1. Density; 2. Correction

Figure 7 shows the dependence of the density of certain fuels on temperature in the range from -60°C to $+200^{\circ}\text{C}$ (density at high temperature is of interest in connection with the heating up of the fuel at high flying speeds).

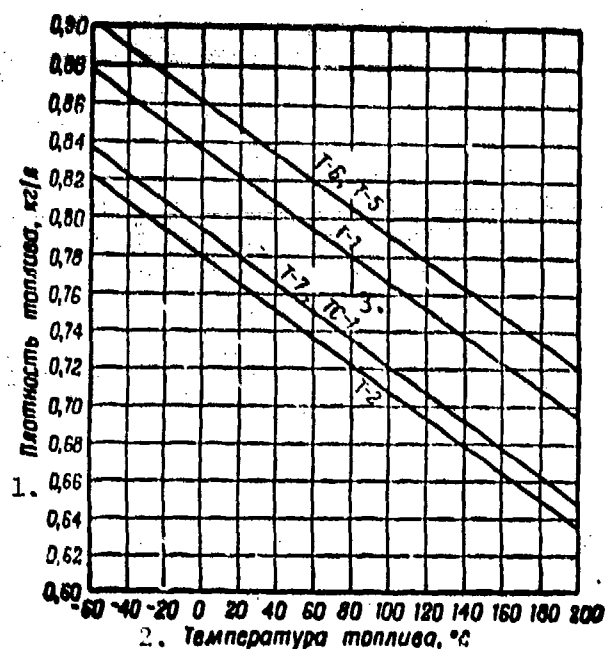


Fig. 7. Change in the density of certain fuels over a wide temperature range. Key:

1. Fuel density, kg/l; 2. Fuel temperature, $^{\circ}\text{C}$.
3. TS-1.

In technical specifications, the density standards are established at 20°C (see Fig. 12). In fuel certificates describing fuel quality, density is also indicated at a fuel temperature of 20°C . If density ρ_4^t at another temperature t is known, from its value one can calculate the density at 20°C (i.e., reduce the actual density to standard conditions) by using the formula

$$\rho_4^{20} = \rho_4^t + \gamma(t - 20). \quad (1.15)$$

Under field conditions and in military laboratories, an areometer is used for measuring density (Fig. 8). Its equilibrium according to Archimedes' law is reached when the weight of the liquid displaced by the immersed portion of the areometer is equal to the specific gravity of the areometer. Therefore, its immersion in a lighter liquid is deeper. The division on the areometer stem corresponding to the upper edge of the meniscus indicates the actual density (the usual reading accuracy is three decimal places) [64].

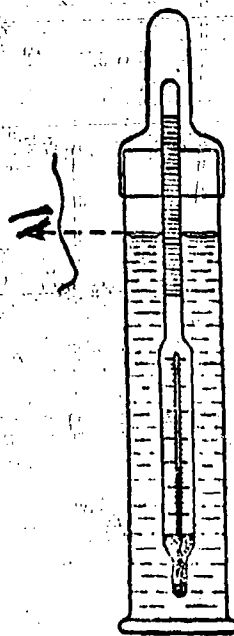


Fig. 8. Density measurement with an areometer.

Viscosity

Viscosity is the property of a liquid to resist the displacement or slip of its layers. Viscosity is the internal friction between the particles of the liquid, caused by molecular cohesion and exchange of momentum. The tangential force of

internal friction F per unit area S during the displacement of one layer of liquid relative to another (i.e., the tangential stress of the liquid) is proportional to the transverse velocity gradient $\frac{dv}{dn}$:

$$\frac{F}{S} = \mu \frac{dv}{dn} \quad (1.16)$$

The transverse velocity gradient expresses the velocity change per unit length in the direction perpendicular to the direction of motion or to the velocity vector (Fig. 9); its units are $\frac{\text{m/sec}}{\text{m}} = \text{sec}^{-1}$.

The proportionality coefficient μ , dependent on the nature of the liquid, is called the dynamic viscosity. Its unit, the poise, corresponds to a resisting force of 1 dyne, arising from the mutual displacement of liquid layers with an area of 1 cm^2 at a rate of 1 cm/sec , separated by a distance of 1 cm from one another (Fig. 9). $\text{One poise} = 1 \text{ dyne sec/cm}^2 = \frac{1}{98.1 \text{ kg/sec/m}^2} = 0.1 \text{ h sec/m}^2$.

The higher the density of a liquid, the faster it flows, the dynamic viscosity being the same. The viscous properties of a liquid from the standpoint of its mobility are characterized by the kinematic viscosity, equal to the ratio of the dynamic viscosity of the liquid to its density (at the same temperature):

$$\nu_t = \frac{\mu_t}{\rho_t} \quad (1.17)$$

The unit of kinematic viscosity, the stoke (abbreviated S), corresponds to a dynamic viscosity of 1 p at a density of 1 g/cm^3 ; $1 \text{ S} = 1 \text{ cm}^2/\text{sec}$. The unit usually employed is 1/100 of a stoke, the centistoke (abbreviated cS). Water at 20.2°C has a viscosity of 1 cS.

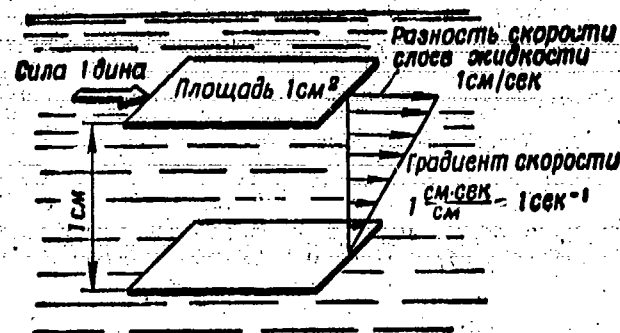


Fig. 9. Diagram referring to the definition of the concept of dynamic viscosity and metric units of viscosity. Key:

1. Force of 1 dyne; 2. Difference in the velocity of liquid layers 1 cm/sec;
3. Velocity gradient; 4. $1 \frac{\text{cm/sec}}{\text{cm}} = 1 \text{ sec}^{-1}$
5. Area, 1 cm²; 6. 1 cm.

Kinematic viscosity in military laboratories is determined with a capillary viscometer from the time τ necessary for a given volume of liquid to flow from the bulb of the viscometer through the capillary (Fig. 10). The calculation is made with the formula $\nu = C\tau$, where C is the viscometer constant, known from its calibration with distilled water at 20.2°C ($C = \frac{1}{\tau_{\text{water}}}$) or some other chemically pure liquid with an accurately known viscosity.

Viscosity changes appreciably with changing temperature of liquids. Therefore, the viscosity norms for each product are established by standards and are recorded in the certificate at a given testing temperature (for fuels, usually at 20°C); the kinematic viscosity at this temperature is denoted by ν_{20} . As the temperature of the liquid decreases, its viscosity increases more markedly the lower the temperature [63, 64].

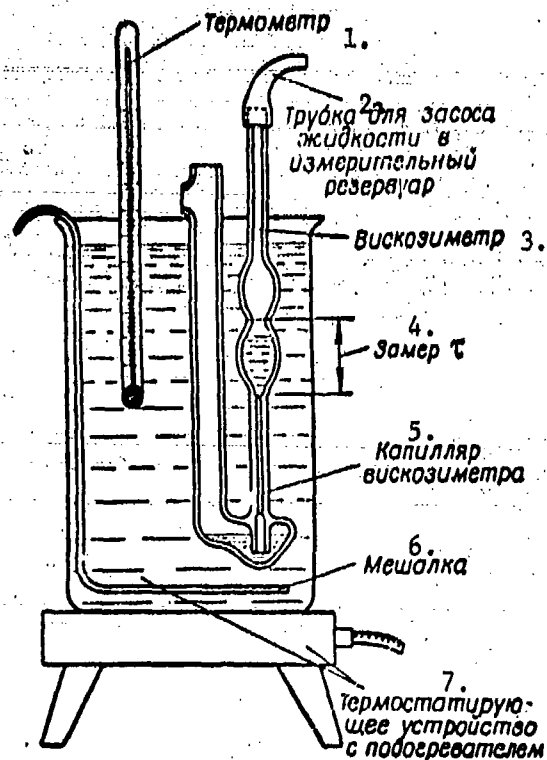


Fig. 10. Diagram of apparatus with capillary viscometer for determining kinematic viscosity. Key:

1. Thermometer; 2. Tube for drawing the liquid into the measuring reservoir; 3. Viscometer; 4. Measurement of τ ; 5. Viscometer capillary; 6. Stirrer; 7. Thermostat with heater.

Vaporizability

The vaporizability of a liquid is its ability to pass to the vapor and gaseous state. It is characterized by the saturated vapor pressure, boiling point (for chemically homogenous liquids), and fractional composition (for liquids of complex composition). In addition, the vaporizability is estimated from the flash point.

Vaporization takes place at any temperature. Its internal mechanism consists in the fact that the fastest molecules of the liquid overcome the forces of cohesion with the neighboring molecules and break out of the mass of the liquid. The higher the temperature, the greater the number of such molecules. If the vaporization takes place from an open volume, almost all the molecules which have passed to the vapor phase are removed from the liquid surface and do not return. If however the vaporization takes place in a closed space, part of the molecules from the accumulated vapor strike the surface of the liquid and return to the latter. In the presence of a certain amount of vapor above the liquid, saturation, i.e., a dynamic equilibrium, takes place: the number of molecules leaving the confines of the liquid becomes equal to the number of returning molecules. The visible vaporization process ceases, the amount of vapor ceases to increase, and hence, the highest pressure possible at the given temperature is established. This maximum pressure is called the saturated vapor pressure. It is determined at a conventional temperature of 38°C from the reading of a manometer attached to a special instrument in which vaporization takes place. Fuels with a higher saturated vapor pressure vaporize faster, and in particular, have better starting qualities. However, at a high saturated vapor pressure, vapor lock obstructing the pumping of the fuel may be formed in the suction lines, and a considerable loss of fuel from the tanks may also occur.

The higher the temperature, the higher the saturated vapor pressure, since vaporization proceeds more vigorously and is balanced by the reverse process only when the vapor has accumulated in sufficient quantity. When the saturated vapor pressure reaches the value of the external (atmospheric) pressure, boiling takes place, i.e., a rapid transition from liquid to vapor not only from the

surface but also from inside the volume of the liquid. The corresponding temperature is known as the boiling point. In the course of boiling, the temperature of a chemically homogeneous liquid remains unchanged if the pressure above the liquid is constant. As the external pressure decreases, the boiling point falls. For this reason, the fuel in the tanks of an aircraft, for example, may start to boil at a high altitude. As the external pressure increases, the boiling point rises. This makes it possible to store in the liquid state and at high pressure substances which at ordinary atmospheric pressure are gases (for example, hydrocarbon gases, carbon dioxide).

In the course of boiling of a petroleum fuel constituting a homogeneous mixture (solution) of chemically different substances, the temperature does not remain constant. At first, mainly the components with high saturation vapor pressures vaporize. The vapor pressure of the remaining liquid is lower, and hence, boiling continues only as the temperature is raised. The temperature of the start of boiling of the fuel is higher than that of the lowest-boiling of its components. During vaporization, the low-boiling substances carry the high-boiling ones over with them, and therefore the temperature of the end of boiling is lower than that of the highest-boiling substance. The vaporizability of such a fuel is characterized by the fractional composition, i.e., by the boiling ranges of the different volume fractions of the fuel. The usual characteristic points of the fractional composition are the temperature of the start of boiling, the boiling ranges of 10%, 50%, and 90% of the fuel volume, and the temperature of the end of boiling (or of boiling of 97.5-98% of the fuel). They are usually regulated by standards and indicated in the certificates for the fuel.

The fractional composition is determined by distilling the fuel (the apparatus is shown in Fig. 11). The graph of the distillation is represented as a relation

between the percentage of the boiling liquid and the temperature (Fig. 12). The steeper the distillation curve, the more homogeneous the fuel. Fractional composition is used to check the process of fuel production. In certain engines, fractional composition is reflected in the performance characteristics of the fuel, in particular, in the combustion efficiency and tendency to form carbon deposits.

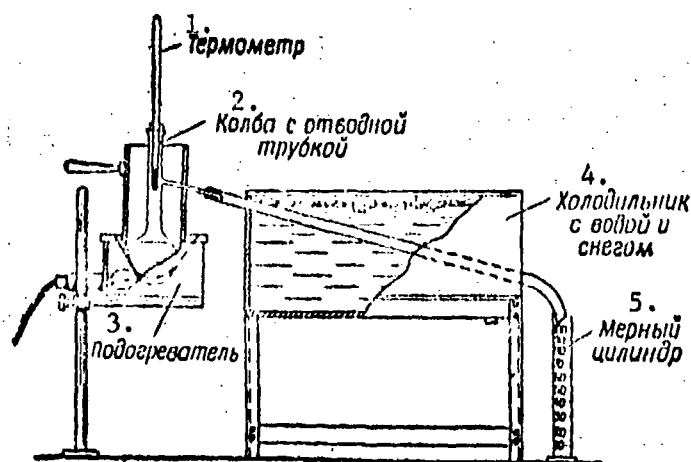


Figure 11. Apparatus for determining the fractional composition of a fuel. Key:

- 1. Thermometer; 2. Flask with side arm; 3. Heater;
- 4. Cooler with water and ice; 5. Graduated cylinder.

In addition to direct measurement, the vaporizability of a fuel is determined by a simple, indirect method, i.e., from the flash point. The fuel is heated in a closed crucible, and its vapor is mixed with the air present therein. As long as the concentration is insufficient, a burning wick will not produce ignition. The flash point is the minimum temperature to which a liquid must be heated so that the vapor above its surface is ignited by a flame brought in contact with it. The lower this temperature, the more easily the liquid vaporizes [39, 60, 64].

Freezing

In a cooled liquid, crystallization begins at a certain temperature. If the liquid is chemically homogeneous, its crystallization takes place at a constant temperature characteristic for it, i.e., the freezing temperature, despite the cooling (removal of heat). This is explained by the liberation of thermal energy in the course of crystallization. Usually, the freezing point coincides with the melting point of crystals. However, supercooling of the liquid occasionally takes place, i.e., crystallization begins at a temperature below the melting point of the crystals (sometimes several tens of degrees lower).

Fuel whose ingredients are infinitely soluble in one another (for example, a mixture of hydrocarbons) crystallizes, not at a constant temperature, but gradually as the temperature falls. Substances with high freezing points crystallize first, followed by those with lower freezing points. At the same time, the temperature of appearance of the first crystals is lower than the freezing point of the substance that freezes most easily (the lower, the less of this substance is present). In low-freezing fuel, the presence of a small amount of hydrocarbons with a high, even positive freezing temperature (benzene, cyclohexane) is not dangerous, i.e., they do not crystallize out of the solution down to low temperatures.

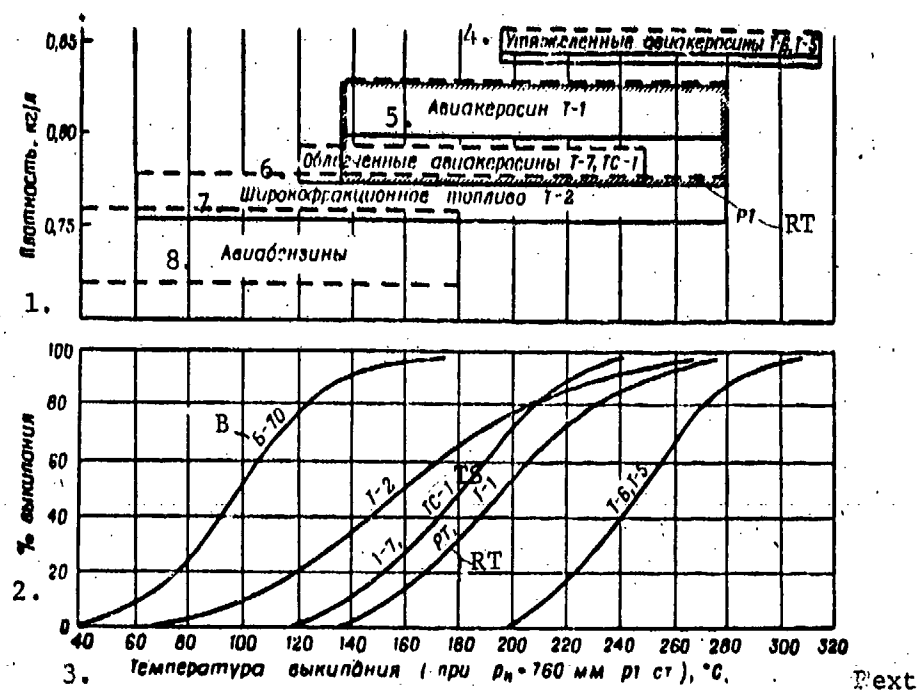


Fig. 12. Density ranges, boiling limits and curves of fractional composition of certain fuels. Key:

1. Density, kg/l; 2. % boiled away; 3. Boiling point (at $p = 760$ Torr), $^{\circ}\text{C}$; 4. T-6, T-5 heavy aviation kerosenes; 5. T-1 aviation kerosene; 6. T-7, TS-1 light aviation kerosenes; 7. T-2 wide-fraction fuel; 8. Aviation gasolines.

The appearance of even isolated crystals in the fuel may have dangerous consequences. The temperature of the start of crystallization is therefore determined, this being the temperature at which the very first crystals are detected by the unaided eye in the course of cooling of the fuel.

On solidifying, the components of certain liquid solutions (for example, of the oxidizers nitrogen tetroxide - nitric acid, hydrogen peroxide - water) turn out to be insoluble or sparingly soluble in one another. At a certain percentage composition, the freezing point of such a solution turns out to be the lowest (much lower than the freezing point of each individual substance making up the solution; see Fig. 31). This composition is called a eutectic. Low-freezing fuels and fuel components are prepared from substances with higher freezing points by using this property of solutions [39, 60, 64].

Physical Homogeneity

Liquid fuels which cannot be separated into their components by mechanical means (standing, filtering, centrifuging) are considered to be physically homogeneous. The inhomogeneous elements of a fuel are mechanical impurities, droplets of water or a water emulsion, or ice crystals (in the form of snowflakes suspended in the fuel).

Mechanical impurities in a fuel are solids forming a precipitate or present in the suspended state (dust or technological impurities, products of corrosion and friction wear of metals, deterioration of hoses, gaskets and filters, oxidation and decomposition of hydrocarbons and other organic substances). The particle sizes vary widely. One liter of practically pure fuel used for filling airplanes contains about 1000 particles measuring around 25μ , hundreds of thousands of particles measuring $5-25\mu$, and many millions of still finer particles, of the order of $1-5\mu$. When the fuel poured into a glass cylinder is inspected, the eye distinguishes particles no smaller than $25-30\mu$ in bright transmitted light (with lateral illumination). Particles larger than 50μ are clearly observed. Particles starting at $5-10\mu$ in size, but in large quantities, not individual ones, are usually considered harmful to fuel equipment. It would seem that visual control of mechanical impurities is useless. This, however, is not correct, since the character of particle size distribution approximately remains valid. If the fuel is found to contain particles visible to the unaided eye, this indicates the presence of an inadmissibly large number of fine, invisible particles.

Quantitative control of mechanical impurities in the fuel is carried out by filtering through nitrocellulose filters, which retain practically all the

particles greater than 0.5μ . A content of mechanical impurities in amounts of 0.0002-0.0003% (2-3g per ton of fuel) is considered safe.

Water that has entered the fuel as a result of dissolution of water vapor from the atmosphere (hygroscopicity of the fuel) or formation of dew and frost in the fuel tanks may be present in dissolved or undissolved form. In hydrocarbon fuels, the excess water over the solubility limit is detected visually with sufficient reliability. The fuel containing undissolved water as a fine emulsion has a turbid appearance; a water residue then appears therein. Crystals of frozen water (a fine suspension of ice) are clearly visible when the cylinder is viewed in transmitted light. Dissolved water is not visible in the fuel, but it disturbs the physical homogeneity of the fuel. Its amount is determined, if necessary, by reaction with calcium hydride (CaH_2), which evolves hydrogen (its volume is proportional to the water content). The majority of nonhydrocarbon components of rocket fuel are capable of dissolving water in substantial quantities but the water cannot cause physical inhomogeneity therein [60, 64, 85, 98, 99].

BASIC INDICES OF CHEMICAL PROPERTIES OF LIQUID FUELS

Chemical Processes

By chemical properties of fuels is meant their tendency to be chemically transformed under conditions characteristic of storage and technical operation, and to react chemically with other substances which are in contact with the fuel. In contrast to physical properties, chemical properties are related to changes in the composition and structure of the molecules of both the fuels and the substances with which they come in contact.

The most important chemical processes for liquid fuels are slow oxidation, decomposition, polymerization and condensation at ordinary temperatures (prior to use) and at high temperatures (during operation of engine); corrosion of metals and nonmetallic materials (rubber, plastics, cloth). In each temperature range certain specific chemical processes predominate, and the remaining stay insignificant [63, 73].

Chemical Stability

The ability of a fuel to remain chemically unchanged and not to react with other substances (of course, before entering the combustion chamber) is called chemical stability. Completely stable fuels do not exist, but paraffinic, naphtenic and to a considerable extent aromatic hydrocarbons, which make up petroleum fuels, are for practical purposes stable. Unstable hydrocarbons are the unsaturated ones, or olefins, which in the majority of petroleum fuels are present in small amounts (up to 2.5%), as well as admixtures of heteroorganic compounds, whose composition includes sulfur, nitrogen, oxygen, or other elements in addition to carbon and hydrogen.

Unsaturated hydrocarbons readily add oxygen, polymerize, and convert into organic acids, resins, and other complex organic compounds. At high temperatures (of the order of 150°C,) they form solid insoluble deposits with other heteroorganic impurities. The content of unsaturated hydrocarbons during analysis of the fuel is determined from the iodine number (weight of iodine in grams which adds to unsaturated hydrocarbons per 100 g of fuel). The percentage of unsaturated hydrocarbons in kerosenes is approximately equal to 0.7 of the iodine number, and in gasolines, to 0.4 of the iodine number.

A direct indicator of the gumming tendency of a fuel is its content of actual gum, i.e., the number of milligrams of solid or semisolid involatile substances remaining after the evaporation of 100 ml of fuel under a stream of air or superheated steam (on

heating to 180°C for kerosene and to 150° for gasoline) [60, 64, 72].

Thermal Stability

Chemical stability at high temperatures is called thermal stability. Its evaluation is made under static and dynamic conditions. Under static conditions, the fuel is tested in sealed flasks at 150°C with a phosphorus bronze plate (standard fuels give the maximum amount of solid residue). The duration of the test for some fuels is 4 hours, and for other, more stable fuels, 5 hours. The filtered residue is determined in milligrams per 100 ml of fuel. Testing under dynamic conditions is carried out by pumping the fuel, which is initially warmed up in the tank of the testing equipment, then in a tubular element. The estimate is made from deposits inside the tubular element and from the pressure differential at the filter. Despite the considerable amount of attention given to problems of thermal stability, the methods used for its estimation inadequately characterize the fuels with reference to actual conditions [58, 60, 64, 72, 95].

Corrosive Properties

Hydrocarbons included in the composition of kerosenes and gasolines¹ are not corrosive; carriers of corrosiveness are inorganic and heteroorganic impurities. The most dangerous is the presence in the fuel of inorganic water-soluble acids and alkalis (which may remain in the fuel as a result of inadequate alkaline treatment and insufficient rinsing following leaching during the production process), insoluble water, free sulfur, and hydrogen sulfide. Their presence in hydrocarbon fuels is inadmissible.

¹Concerning the corrosiveness of rocket fuel components, see Ch. 5.

Water-soluble acids and alkalis, and water, which almost always contains a certain amount of dissolved salts, are electrolytes (electrically conducting liquids) and constitute a medium in which electrochemical corrosion of metals develops. A potential difference arises on droplets of electrolytes adjacent to a metal surface, which is always slightly inhomogenous in composition. Under the influence of this potential difference, positively charged ions break away from the metal surface. When they come in contact with negatively charged hydroxyl ions OH or acid residues, corrosion products are formed. The metal surface becomes rough, and seizing may occur in the friction parts of fuel equipment.

Precipitating corrosion products obstruct filters, fuel equipment, and control devices.

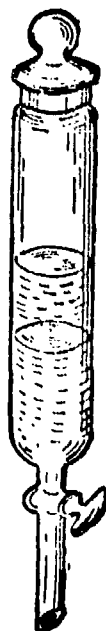


Fig. 13. Separatory funnel.

During quality control, water-soluble acids and alkalis are observed by shaking a warmed fuel together with warmed water (10:1) in a separatory funnel (Fig. 13). The water extract (bottom layer in the funnel) is drained and checked with indicators: methyl orange (in the presence of acid, it changes from yellow to pink) and phenolphthalein (in the presence of alkali, it turns from colorless to purple). To make sure that alkaline compounds are absent, it is recommended that 100 ml of the water extract be shaken with 300 ml of fuel, then the indicator be introduced, and the water extract be evaporated down to 10 ml.

Organic acids which are incompletely removed from the fuel during its production and which form in it during extended storage produce a soapy residue with copper and iron alloys. The acidity of the fuel is expressed in numbers of milligrams of potassium hydroxide (KOH) which neutralizes (converts into soaps and other salts) the acids present in 100 ml of fuel.

Free (elemental) sulfur present in the fuel causes corrosion of copper alloys. It may be observed by testing on a copper plate, which is immersed for three hours in a fuel heated to 50 or 100°C. In the presence of sulfur, a polished plate becomes stained. For hydrocarbons jet fuels, a change in the color of the plate is inadmissible. Hydrogen sulfide, which is also inadmissible, is detected by a special test on lead paper.

Among organic compounds of sulfur the most dangerous are mercaptans (C_nH_mSH), heavy liquids with a pungent, unpleasant odor. They form slimy precipitates, mercaptides, with nonferrous metals. Mercaptans are particularly active under high humidity conditions. The content of mercaptan sulfur is determined in mili-

laboratories from the amount of the blue ammonia solution of copper sulfate which has not reacted with the fuel (until the solution ceases to be bleached).

This reaction does not detect all the mercaptans. An accurate determination is made by potentiometric titration.

Other sulfur compounds in fuels do not cause metal corrosion directly. However, sulfur dioxide SO_2 formed by their combustion at high temperature reacts with metals, and on cooling in a mixture with atmospheric oxygen and moisture, may change into corrosive sulfuric acid. $\text{SO}_2 + \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$ The total sulfur content is found by burning the fuel and determining the amount of sulfur dioxide in the combustion products.

The destruction of heat-resisting alloys in contact with fuel combustion products may be promoted by the presence in the fuel of negligibly slight quantities (thousandths of a percent) of vanadium, molybdenum, and some other metals; their source may be both the initial petroleum and the catalysts employed in fuel production. Oxides of these metals serve as catalysts of gas corrosion.

Hydrocarbons may cause swelling, and in time, destruction of ordinary (not resistant to gasoline) grades of rubber and other materials from which seals are made. They penetrate into microscopic pores and slowly dissolve these materials the process of softening and deterioration usually takes place at once to a considerable depth. Aromatic hydrocarbons have a particularly marked effect on rubber and leather. For this reason, rubber parts and seals used in fuel systems are made of special (oil-resistant) grades of rubber [64, 72, 116].

GENERAL FUEL REQUIREMENTS

Parameters and Processes Affected by Fuel

The quality of a fuel determines to some extent the ease of starting of an engine, its rate of warmup and acceleration (response), the thrust (or power) developed by the engine, its economy, the stability of its operation, and its reliability in the course of the specified service life. Under any service conditions, the fuel should permit an optimum course of the process of feeding, mixing, combustion, and elimination of the combustion products from the engine without causing wear or overheating of the parts, corrosion, or contamination of the engine. It is desirable that the largest possible amount of fuel be contained in a limited fuel tank volume. During transportation, storage, and fueling, stability of the fuel and ease and safety of its handling are of major importance [1, 34, 73, 81].

Requirements Placed on Fuel Properties

The general requirements placed on the energetic and physicochemical properties of fuel may be classified as follows:

- 1) Requirements concerning energetic properties:
 - a) high calorific value;
 - b) favorable thermodynamic properties of combustion products (stability to thermal dissociation, high heat capacity, absence of condensed substances);

- c) low stoichiometric coefficient (the smallest possible required amount of oxidizer);
 - d) high density, making it possible to have the required on-board reserve of energy and working substance for the engine;
- 2) Requirements concerning the physicochemical properties which provide for operation of the engine:
- a) moderate viscosity (especially at low temperatures) ensuring an adequate atomization of the fuel when the latter enters the combustion chamber;
 - b) optimum vaporizability (boiling point or fractional composition and saturated vapor pressure) sufficient for an adequate carburation before the combustion, and also during starting, but causing no cavitation in the fuel system;
 - c) sufficiently intense and simultaneously uniform and stable combustion without knock or a dangerous vibration level;
 - d) high combustion efficiency;
- 3) Requirements concerning the physicochemical properties affecting the reliability of operation and service life of the engine and fuel system:
- a) low temperature of the start of crystallization;
 - b) physical homogeneity (absence of solid inclusions, i.e., mechanical impurities, and absence of emulsion water);
 - c) adequate lubricating properties (surface activity) preventing the destruction or rapid wear of friction parts of the fuel apparatus;
 - d) absence or safe level of corrosive action on metals and destructive action on other materials (rubber, plastics) by both the fuel and its combustion products;

- e) absence of chemically unstable components which tend to be converted into solid or high-viscosity (gummy) deposits in the fuel system;
 - f) low flame emissivity (to avoid a dangerous heating of the combustion chamber walls);
 - g) absence of carbon deposition.
4. Requirements concerning physicochemical properties ensuring combat readiness, convenience of handling and safety of personnel:
- a) low solidification temperature ensuring the possibility of pumping and fueling under severely cold conditions;
 - b) high boiling point or high flash point, promoting a decrease of losses during storage and a decrease of fire hazards;
 - c) chemical stability during prolonged storage;
 - d) low hygroscopicity (no tendency to absorb moisture from air);
 - e) nonexplosivity;
 - f) low toxicity level of the liquid fuel, its vapor and its combustion products (1, 60, 73].

Fuel-Engine Compatibility

In addition to the general requirements corresponding to the conditions of their use in special types of engines may be imposed on fuels, for example, self-ignition when the combustible comes in contact with the oxidizer in liquid fuel engines; a high heat capacity when the fuel is used as the cooling liquid in the jacket of the LFE combustion chamber. However, each of the general requirements has a different importance in engines of different types.

Usually, real fuels do not possess all of the desirable properties. For each fuel, strict requirements are imposed only with regard to the properties that are decisive for its use in engines of a given type. Only minimum requirements or no requirements are placed on the remaining, less important properties. At the same time, it is kept in mind that the fuel must be as inexpensive and as readily available as possible. [81, 107].

CHAPTER 2

BRIEF DATA ON THE PRODUCTION OF FUELS

PETROLEUM - THE BASIC RAW MATERIAL IN FUEL PRODUCTION

Reserves and Production

Practically all of aviation fuel and certain combustible components of rocket fuel are prepared from petroleum.¹ The identified petroleum reserves in various regions of the world increase from year to year. Apparently, the petroleum reserves of the earth constitute hundreds of billions of tons, a considerable portion being located on the territory of the Soviet Union. Although the world production of petroleum exceeds 2 billion tons per year, there is no danger of exhausting the petroleum reserves for at least several decades.

In the USSR, petroleum production and refining are increasing at rapid rates. In the last 20 years, petroleum production has increased more than tenfold and in 1970 reached 353 million tons; during the current five year period it will exceed the half billion mark. The bulk of the petroleum comes from the Volga-Ural deposits (about 3/4 of the total production), the regions of Baku and Groznyy, western Kazakhstan, and Turkmenistan; petroleum production is developing in the western Siberian petroleum deposits, the largest in the country.

¹The production of aviation fuel from coal and other solid combustibles costs much more than that from petroleum, and has been practically discontinued (with the exception of a few foreign plants).

Petroleum Refining

Petroleum consists of hydrocarbons of varied structure with different boiling temperatures, a certain quantity of heteroorganic compounds containing oxygen, sulfur, nitrogen, as well as inorganic impurities of sulfur, salts, etc. There are two methods of refining petroleum into motor fuel. The first consists in separating hydrocarbon fractions with suitable physicochemical properties and removing noxious impurities. The second method consists in chemically processing the hydrocarbons and altering their composition and structure for the purpose of imparting the required physicochemical properties to the fuel, i.e., preparing hydrocarbon fractions which either were not present in the petroleum at all, or were present in small quantities.

At the present time, the bulk of aviation fuel is produced by the first method, and the second method is used mainly to produce individual fuel components. The required properties are imparted to the fuel by producing it from a suitably chosen crude (petroleum of given deposit) and using a suitable process, mixing the components, and introducing additives. The quality of the crude and the method of production sometimes cause certain undesirable properties of the fuel that must be considered in its application, for example, the corrosive activity of fuels from sulfur-containing Volga-Ural crudes, insufficient thermal stability of fuels from Baku crudes, or low antiwear properties of the fuels following hydrofining.

The second method, which eliminates the dependence of fuel quality on the nature of the crude, is assuming an increasing importance with increasing strictness of fuel requirements as a result of higher temperatures and other unfavorable operating conditions of aviation equipment [60, 62].

STRAIGHT-RUN DISTILLATION OF PETROLEUM

Operation of Pipe Still

The primary process of petroleum refining is straight-run distillation. It consists of a physical separation of the petroleum into fractions with different boiling ranges. The distillation is carried out in pipe stills (Fig. 14.) The petroleum, heated to 300-330°C in heat exchangers and in a pipe furnace, enters a fractionating column in the form of a steel tower 15-30 m high with transverse partitions, i.e., plates, where its light fraction evaporates; the remaining residue (fuel oil) flows into the bottom part of the column.

The petroleum vapors rise in the column, cool off, and gradually condense on the plates, forming distillates of various compositions. Diesel fuel with a comparatively high boiling temperature is collected from plates of the middle section of the column, and jet fuel distillate of lower boiling temperature is collected from the upper, colder plates. The lowest-boiling petroleum fractions leave the column from its upper section and are carried by pipes into coolers; they are used to condense the gasoline distillate and to separate hydrocarbon gases. To maintain the required temperature difference, the upper section of the column is cooled by refluxing, i.e., returning part of the gasoline in liquid form, while individual plates of the lower and middle sections are heated with superheated steam [60].

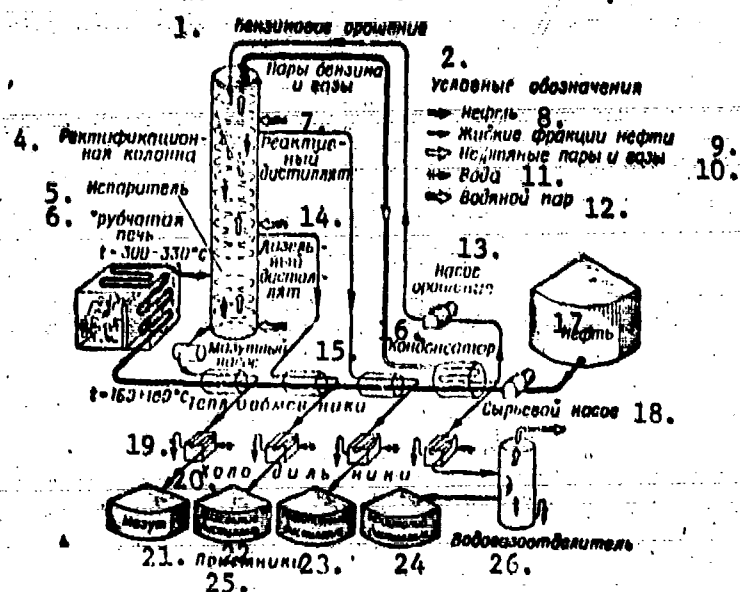


Fig. 14. Diagram of petroleum refining pipe still. Key:

1. Gasoline refluxing; 2. Notation; 3. Gasoline vapors and passes; 4. Fractionating column; 5. Vaporizer; 6. Pipe furnace; 7. Jet fuel distillate; 8. Petroleum; 9. Liquid petroleum fractions; 10. Petroleum vapors and gases; 11. Water; 12. Steam; 13. Refluxing pump; 14. Diesel distillate; 15. Fuel oil pump; 16. Condenser; 17. Petroleum; 18. Stock pump; 19. Heat exchangers; 20. Coolers; 21. Fuel oil; 22. Diesel distillate; 23. Jet fuel distillate; 24. Gasoline distillate; 25. Receivers; 26. Water-gas separator.

Straight-run distillation usually yields an average of 10-15% gasoline, 15-20% jet fuel or kerosene, 15-20% diesel fuel, and about 50% fuel oil. The annual output of a modern pipe still amounts to several million tons of petroleum per year [60, 62, 68].

PURIFICATION AND PROCESSING OF PETROLEUM PRODUCTS

Chemical Purification

Purification of distillates involving the removal of harmful impurities having mostly acidic properties is carried out by using an alkali, i.e., a caustic

soda solution. If the distillate contains a significant quantity of gum and sulfur and nitrogen substances, it is subjected to treatment with 92-93% sulfuric acid, with which they react and precipitate out. After the purification, the fuel is washed with water.

The most reliable method of removing sulfur compounds (large quantities of which are present in Ural-Volga crudes) involves catalytic hydrofining of petroleum products (purification with hydrogen). At a pressure of 50-70 atmospheres and a temperature of the order of 400°C, hydrogen mixed with distillate vapor combines with the sulfur present in the latter, forming hydrogen sulfide. Hydrogen sulfide is subsequently driven out of the distillate by alkaline purification. Hydrofining also involves addition of hydrogen to unsaturated hydrocarbons and their transformation into saturated ones, so that the stability of the fuel increases. The content of the most harmful sulfur compounds, mercaptans, may also be decreased by their catalytic transformation into inactive disulfides (without a decrease of the total sulfur content) according to the reaction, $2 \text{RSH} + 1/2 \text{O}_2 \rightarrow \text{RSSR} + \text{H}_2\text{O}$; this form of refining is called demercaptanization [60, 61].

Deparaffinization

In order to lower the solidification temperature of aviation fuels, the latter are sometimes subjected to a special form of refining, i.e., treatment with carbamide (urea), $\text{CO}(\text{NH}_2)_2$. To the latter are added high-melting paraffin hydrocarbons. A suspension forms in the fuel and is subsequently filtered out.

If they meet suitable technical requirements, the purified products of straight-run distillation of crude constitute ready motor fuels. If necessary,

they are improved by adding components and additives which make it possible to obtain fuels with the necessary characteristics. Fractions unsuitable as fuels are subjected to chemical processing [60].

Thermal Cracking

The simplest form of chemical processing of heavy petroleum fractions (mainly fuel oil), but unsuitable because of the low quality of the products obtained, is thermal cracking. Cracking essentially consists in splitting large molecules into smaller ones under the influence of high temperature (about 500°C). It is carried out at a pressure of several tens of atmospheres. The yield of light petroleum products such as gasoline and kerosene from thermal cracking may be of the order of 50%; they contain many unsaturated hydrocarbons and are therefore unstable. A better fuel quality is obtained by more complex and expensive catalytic processes [60, 89].

Catalytic Processing

Catalytic cracking is usually carried out in columns filled with a solid powdered catalyst at a temperature of about 500°C and a pressure of several atmospheres. Simultaneously with the splitting of large hydrocarbon molecules, there take place polymerization processes, i.e., combinations of small molecules into new structures, redistribution of hydrogen with the formation of aromatic hydrocarbons and isoparaffins, etc. Catalytic reforming on an aluminum-platinum catalyst converts naphthenic hydrocarbons into aromatic ones ($C_nH_{2n} - C_nH_{2n-6} + 3H_2$). It is carried out mainly for the purpose of increasing the antiknock value of gasolines, but it simultaneously produces cheap hydrogen.

On the contrary, catalytic hydrocracking conducted in a hydrogen medium at 50-150 atmospheres converts polycyclic aromatic hydrocarbons into stable naphthenes, which are useful as ingredients in the composition of jet fuels. Upon adding hydrogen, unsaturated hydrocarbons convert into paraffinic and iso-paraffinic ones, and sulfur compounds are removed, as in hydrofining.

Individual components necessary for improving the antiknock value and vaporizability of aviation gasolines, increasing the density and calorific value of jet fuels, and certain combustible components of rocket fuels are produced by means of catalytic processes of hydrogenation, alkylation, and isomerization of light hydrocarbons, mainly reactive unsaturated cracking gases. Molecules with a certain structure imparting the required properties to the fuel are thus obtained. Polymerization of unsaturated gases can be used to obtain the required structure of molecules of both the liquid fuels and rubberlike polymers used as combustibles and binders in the composition of solid rocket fuels [28, 61, 82, 123].

PRINCIPLES OF PRODUCTION OF NONHYDROCARBON FUELS AND COMPONENTS

Preparation of Hydrogen

Hydrogen is obtained by various methods from methane (or other natural hydrocarbon gases) by the thermal decomposition $\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2$, partial oxidation $\text{CH}_4 + 1/2 \text{O}_2 \rightarrow \text{CO} + 2\text{H}_2$, reaction with steam (conversion) $\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$, passing steam over incandescent coal $\text{C} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}$, and reaction of steam with carbon monoxide $\text{H}_2\text{O} + \text{CO} \rightarrow \text{CO}_2 + \text{H}_2$. Most of these processes are reversible and produce a substantial yield only at a temperature of the order of 1000°C in the presence of catalysts, so that these processes are expensive. A cheaper

hydrogen is obtained from cracking gases, particularly those formed in catalytic reforming and hydrocracking of petroleum distillates, and also from coke gas. When cheap electric power is available, hydrogen may be obtained by electrolyzing water. Liquefaction of hydrogen is carried out by first compressing the gas, deep cooling with liquid nitrogen, and expanding while removing the mechanical energy and heat of condensation. Immediately before liquefaction at temperatures of minus 210-253°C, a catalyst (iron hydroxide) is used to carry out the process of ortho-para transition, since para hydrogen is the thermodynamic equilibrium form at the boiling point of liquid hydrogen, the transition from normal composition to para hydrogen being associated with the liberation of a greater amount of heat (126 kcal/kg) than is required to vaporize hydrogen (108 kcal/kg). If the ortho-para transition is not carried out artificially, during its slow natural course liquid hydrogen will completely evaporate even under conditions of ideal thermal insulation [68, 86].

Production of Oxygen

Oxygen is obtained from liquid air. By alternating compression, cooling and expansion, the temperature of air is gradually brought down to its transition to the liquid state. Then, at a temperature of around -190°C, practically all of the nitrogen evaporates from air (BP -196°C), and liquid oxygen remains (BP -183°C). The isolated nitrogen is used in the production of its compounds and for various technical purposes; for example, it is cooled again and liquefied, then poured into the jacket cavity of tanks with liquid oxygen and other cryogenic components whose boiling points are higher than those of nitrogen [10, 73].

Preparation of Nitrogen-Containing Components

Ammonia is obtained by direct synthesis from nitrogen and hydrogen

$N_2 + 3H_2 \rightarrow 2NH_3$ in a contact unit - a tower filled with catalyst (iron oxides) at temperatures above $500^\circ C$ and pressures of 500-1000 atmospheres. The ammonia formed is separated from the unreacted gaseous mixture by passing the latter through a condenser (the boiling point of liquid ammonia is $-33^\circ C$). The synthesis of ammonia is the basis for the production of all nitrogen compounds. Nitrogen tetroxide and nitric acid are obtained by oxidizing ammonia with air in a contact apparatus with a platinum catalyst. Ammonia is first converted into nitric oxide NO, then into nitrogen dioxide NO_2 , and finally, on cooling below $21^\circ C$, into the liquid tetroxide N_2O_4 . Nitric acid is prepared from nitrogen dioxide by dissolving the latter in water without oxygen or in the presence of oxygen: $3NO_2 + H_2O \rightarrow 2HNO_3 + NO$, or $4NO_2 + 2H_2O + O_2 \rightarrow 4HNO_3$.

Nitroglycerin, nitrocellulose, ammonium nitrate and other nitrates which constitute the components of solid rocket propellants are obtained by reacting concentrated nitric acid with glycerin, cellulose, ammonia solution, etc. Amines, which are used as combustible components of liquid rocket propellants, are obtained in various ways: triethylamine $N(C_2H_5)_3$, by reacting ammonia with ethanol; xylidine $C_6H_3NH_2(CH_3)_2$, by treating xylene with nitric acid and then with hydrogen.

Hydrazine NH_2NH_2 is obtained from ammonia by treatment with hypochlorite:

$2NH_3 + NaOCl \rightarrow N_2H_4 + H_2O + NaCl$; in addition, the production of dimethylhydrazine $N_2H_2(CH_3)_2$ utilizes dimethylamine, $NH(CH_3)_2 + NH_3 + NaOCl \rightarrow N_2H_2(CH_3)_2 + NaCl + H_2O$ [2, 73, 86].

CHAPTER 3

FUELS FOR AIR-BREATHING JET ENGINES (JET FUELS)

CONDITIONS OF USE AND QUALITY REQUIREMENTS OF FUELS FOR GAS TURBINE ENGINES

Types of Fuels

Airplanes and helicopters with gas turbine (turbojet and turboprop) engines constitute the fundamental, most common type of aviation equipment; they must be designed to operate on fuels having plentiful raw material resources and an extensive production base. In order to obtain the maximum possible quantity of energy from the on-board reserve of fuel, which is limited by the capacity of the tanks and by the initial flying weight of the airplane, high calorific value and density requirements are placed on the fuels. Among the mass-produced and cheap types of petroleum fuels, these requirements are best satisfied by kerosenes, which boil between approximately 120 and 280°C (Fig. 12). In addition, wide-cut fuels are also used to a limited extent, i.e., mixtures of kerosene and gasoline (mainly for subsonic planes) which boil at approximately 60-280°C, and heavy kerosenes with boiling limits of 195-315°C for airplanes with high supersonic speeds [60, 80].

Fuel Supply

Many fuel quality requirements are related to the design and operating conditions of the airplane fuel system and engine fuel equipment. In order to avoid cavitation in the airplane fuel system, vapor-air lock, and failures in the

operation of booster and transfer pumps, a limiting norm for the saturated vapor pressure is established for wide-cut fuel (not more than 100 Torr at 38°C). Before entering the engine, the fuel usually passes through a heat exchanger (fuel-oil radiator) where its temperature is raised by 20-40°C, and under certain conditions (for example, when the flying level of the airplane decreases), by 80-100°C. In connection with the heating, in order to avoid the formation of solid residues, the fuel must be thermally stable (it is desirable that the residue does not exceed 10-12 mg per 100 ml). In the future, requirements placed on this index will be raised (in particular, for hydrofined fuels, a norm of not more than 6 mg per 100 ml has been established).

A low-pressure filter is used to protect the pumps and fuel supply regulators from solid particles that randomly enter the fuel system from the outside or as a result of wear. The use of fuel contaminated with mechanical impurities and containing ice crystals or water leads to obstruction of the filter, a decrease of its transmissive capacity, and engine failure. The temperature of the start of crystallization of the fuel should be no higher than -60°C.

The fuel equipment of the engine is made to high tolerances, with clearances of the order of 7-10 μ , and with channels having cross sections of tenth of a millimeter; even slight deposits or corrosion may disrupt its normal operation. For this reason, limits have been placed on the content of actual gum (up to 4-6 mg per 100 ml of fuel) and unsaturated hydrocarbons tending toward gum formation (iodine number no greater than 2-3.5 g, and for hydrofined fuels, no greater than 0.5-1 g per 100 g of fuel, which corresponds to 0.3-2.5% of unsaturated hydrocarbons). Free (elemental) sulfur is inadmissible, and the content of mercaptan sulfur is limited to 0.005%; in the future, this index should be made

stricter. Mercaptan sulfur is practically absent in fuels from low-sulfur crudes; in grades subjected to hydrofining, its content is reduced to 0.001% or less. Corrosive water-soluble acids and alkalis are completely inadmissible. The organic acidity of fuel is not as strictly limited - it must not exceed 0.7-1 mg of KOH per 100 ml, and for hydrofined fuels, 0.5 mg.

The operation of fuel equipment units also depends on the viscosity of the fuel. An increased viscosity causes large loads on the pump, and may slow down the operation of certain regulating devices and reduce the atomization of the fuel by the injector. As the droplet size increases, the fuel injected into the combustion chamber heats up and vaporizes much more slowly, the combustion efficiency decreases, starting becomes poorer, and carbon deposition increases. The viscosity of fuels is limited at the upper end at subzero temperatures, where it is high (Fig. 15). At a positive temperature of +20°C, the viscosity is limited at the lower end mainly from the standpoint of improvement of pump lubrication. However, the lubricating properties of the fuel in the pump apparently depend little on the viscosity; their determining factor is the presence in the fuel of surface-active agents for which no norms are available [35, 60, 80, 112].

Fuel Combustion

The conditions for fuel combustion during normal operation of gas-turbine engines are sufficiently favorable, so that no special requirements are imposed on the vaporizability of the fuel. Most of the fuel injected into the combustion chamber enters the flow of compressed air at a temperature of 200-400°C, or even hotter combustion products drawn toward the injector (Fig. 16), and vaporize.

rapidly. At the boundary of the return flow and of the flows of air entering from the front unit, and particularly through lateral openings, the hot gases are vigorously mixed with the air and fuel vapor and ignite the fuel-air mixture. A cup-shaped or sinuous flame front is formed in which practically all of the fuel manages to burn up in normal operation. Less favorable conditions for vaporization exist during engine starting, since cold air enters the combustion chamber. For this reason, the starting fuel used in certain engines is easily vaporizable gasoline.

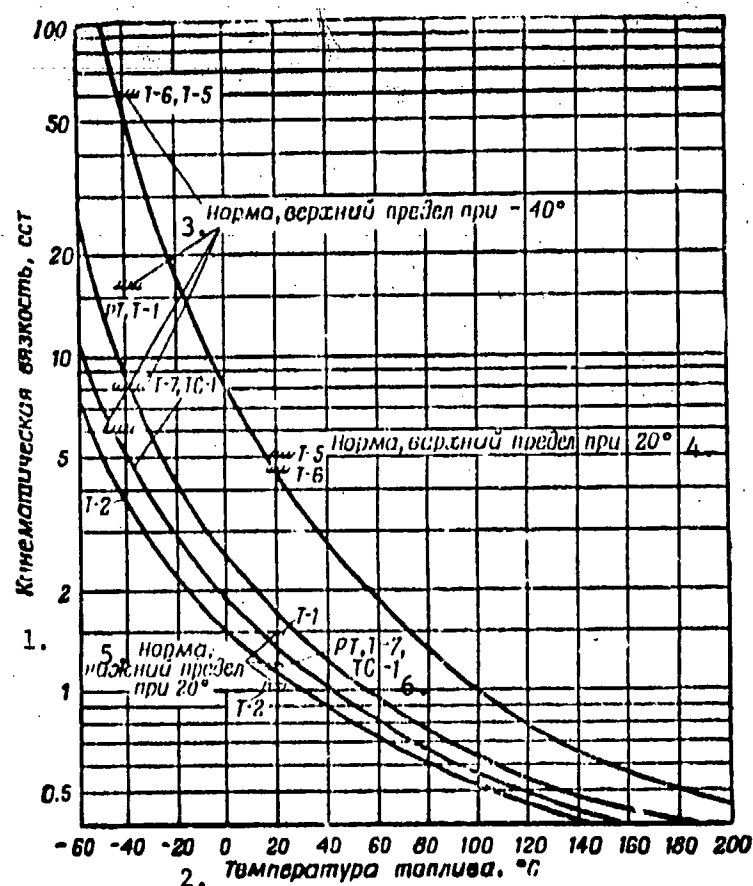


Fig. 15. Viscosity of jet fuels versus temperature. Key:

1. Kinematic viscosity, cS; 2. Fuel temperature, °C;
3. Norm, upper limit at -40°; 4. Norm, upper limit at 20°;
5. Norm, lower limit at 20°; 6. TS-1

Definite requirements regarding the physicochemical properties of a fuel are imposed in order to prevent carbon deposition on parts of the gas circuit of engines; for this purpose, a limit is placed on the content of aromatic hydrocarbons (not more than 10-22%) and height of the nonsmoking flame (not more than 20-25 mm). To avoid the formation of inorganic scale (slag), the ash content of the fuels is limited (to 0.003%). In view of the difficulties of the analysis, no norms have been established for the specific ash impurities causing corrosion of the gas circuit (vanadium oxide, etc.). To avoid gas corrosion, the total sulfur content has been limited to 0.1% in fuels from low-sulfur crudes and to 0.25% in fuels from sulfur crudes. For a fuel system, however, the so-called "total sulfur content" is not harmful, since practically all of this sulfur is included in the composition of unreactive compounds. They are assumed to play a useful role, i.e., as antioxidants and lubricants. For hydrofined fuels, the upper limit of the total sulfur content is 0.05%.

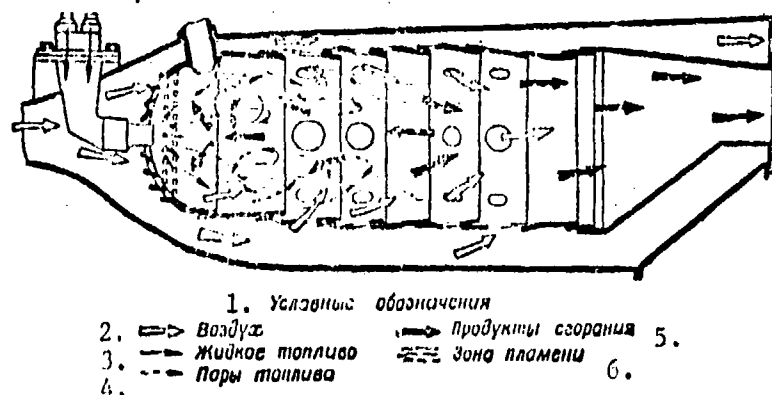


Fig. 16. Diagram of mixing and burning of fuel in the combustion chamber of a gas turbine engine. Key:

1. Symbols; 2. Air; 3. Liquid fuel; 4. Fuel vapor;
5. Combustion product; 6. Flame zone.

Finally, to ensure a greater fire safety, a limitation has been imposed on the vaporizability of light fractions of kerosene type fuel by setting the flash point in the presence of a flame at not below 28-30°C [35, 60, 80].

Effect of Fuel on Engineering Reliability

Fuels for gas turbine engines must first of all meet the requirements which provide for the operational reliability of engines and hence, trouble-free flights.

Figure 17 shows a schematic diagram of the relationship between the properties of a fuel and the types of failures, defects and other abnormal service phenomena, and also the performance data of an airplane and engine. The degree of influence of the various properties of the fuel is not uniform, and in many cases has not yet been clearly determined. Some indices are based on use in certain types of TJE or TPE, and insufficiently on use in other engines. The properties themselves are interrelated, since in the final analysis they are determined only by the chemical composition of the fuel and hence, by the grade of crude, technology of its refining, and additives. Improvement of one set of properties is sometimes associated with worsening of others, and a high level of requirements for all the indices cannot be met in practice. In view of the above, standards have established that fuel for jet engines must correspond in raw material and production technology to the samples that have passed official tests in engines. Correspondence between the commercial products of the petroleum industry and the tested samples serves as an additional guarantee of the operational reliability of the equipment [7, 80, 112].

Caption for Fig. 17.

Fig. 17. Properties of jet fuel affecting the tactical-technical data of an airplane and the operational reliability of its power plant.

Key:

1. Maximum fuel temperature; 1A. on modern airplanes; 1B. on prospective airplanes with cruising speed $M=3$;
2. Fuel quality indices (classified according to parts of the power plant in which their influence is manifested);
3. Parameters, processes and phenomena directly dependent on fuel properties;
4. Dangerous aftereffects and service characteristics which may be caused by unsatisfactory fuel quality;
5. Performance indices of the airplane and engine which may be affected by fuel properties;
6. Fuel tanks;
7. Booster pumps;
8. Heat exchanger;
9. Filter;
10. Regulator pumps;
11. Main combustion chamber;
12. Turbine;
13. Afterburner;
14. Variable nozzle;
15. Gas circuit;
16. Injectors;
17. Gas temperature up to 2200°C ; at entrance to turbine, up to 1400°C (prosp.);
18. Reserve of energy;
19. Weight of fuel;
20. Calorific value;
21. Density;
22. Fuel losses;
23. Boiling or rapid vaporization at altitude;
24. Saturated vapor pressure;
25. Flash point;
26. Solubility of air;
27. Explosion or fire hazard;
28. Formation of explosive mixture;
29. (Ignition);
30. Electrification;
31. (Self-ignition temperature);
32. Dielectric properties;
33. Behavior fluctuations or engine shutdown;
34. Cavitation;
35. Vapor-air lock;
36. Rarefaction at entrance;
37. Saturated vapor pressure, solubility of air;
38. Viscosity (at low temperature);
39. Coefficient of heat transfer from walls to fuel;
40. Thermal conductivity, heat capacity, viscosity;
41. Erosion of pump material;
42. Rise in the temperature conditions of cooled systems (lubrication, etc.);
43. Reduction in the pumping of fuel, decrease in speed of rotation, shutdown of engines;
44. Vapor formation near wall;
45. Saturated vapor pressure;
46. Deposits on walls;
47. Thermal stability;
48. Obstruction by solid particles;
49. Mechanical impurities, thermal stability;
50. Formation of crystals at low temperature;
51. Sticky deposits;
52. Water, anti-icing additive, temperature of start of crystallization;
53. Actual gum, naphthenic soap;
- 53A. Change in engine acceleration and in time of cutin and cutoff of afterburner, sharp behavior fluctuations, surging (change in maximum number of rpm);
57. Surfactants;
38. Water, free sulfur, hydrogen sulfide, mercaptan sulfur, water-soluble acids and alkalis, organic acidity;
59. Lubrication of friction parts of pumps;
60. Liquid corrosion (destruction of surface, formation of solid and gelatinous precipitates);
61. Premature wear, seizing, failure of pumps, breakdown of automatic equipment, decrease in speed of rotation, engine shutdown;
62. Obstruction of channels, nozzles, clearances, etc.;
63. Thermal stability, actual gum, iodine number, mechanical impurities, naphthenic soaps;
64. Density, viscosity, surface tension;
65. Fineness and spray cone;
66. Flaring;
67. Impairment of starting;
68. Behavior instability;
69. Carbon deposition on injector;
70. Vaporization;
71. Carbonization in liquid phase;
72. Carbon deposition on walls;
73. Combustion efficiency;
74. Sooting in the flame;
75. Fractional composition;
76. Aromatic hydrocarbons, luminometric number; height of smoking flame;
77. Ash content;
78. Slag formation;
79. Flame emission;
80. Gaseous corrosion (destruction of surface);
81. Vanadium, molybdenum, total sulfur content (sulfur dioxide in combustion products);
82. Calorific value of combustible mixture;
83. Molecular weight of combustion products (heat capacity and gas constant);
84. Maximum gas temperature;
85. Smoking;
86. Damage to turbine blades and other parts due

to detachment of deposit; 87. Buckling, cracks, failure of combustion chambers; 88. Burnout of combustion chambers, destruction of turbine blades; 89. Dissociation of combustion products; 90. Thermal expansion efficiency; 91. Number of atoms in the molecules of combustion products; 92. Flying weight; 93. Payload; 94. Range and duration of flight; 95. Altitude; 96. Dry thrust; 97. Maximum thrust with afterburning; 98. Specific fuel consumption.

JET FUEL GRADES

Aviation Kerosenes

T-1 fuel, which is obtained mainly from low-sulfur crudes of Baku and Sakahlín, contains a considerable amount of naphthenic hydrocarbons and is characterized by a higher density in comparison with other mass-produced grades of aviation kerosene (according to practical standards, the density at 20°C is at least 0.800, actually, 0.800-0.830).

TS-1 fuel (the letters in its grade designation stand for "sulfur fuel") is most widely employed. TS-1 fuel is produced from the Ural-Volga sulfur crudes, whose reserves and production are several times as high as those of the low-sulfur Baku crudes. TS-1 fuel has a lower density (at least 0.775 at 20°C); it is slightly worse than T-1 fuel in corrosive properties and its effect on the wear of engine fuel pumps; however, TS-1 fuel provides for normal operation during the entire service life of mass-produced engines for which it is designed. Adoption of Siberian low-sulfur crudes will permit the production of TS-1 fuel of the same density as the Ural-Volga fuel, but as good as T-1 in corrosive inertness. The low density of TS-1 fuel is explained by the fact that Ural-Volga and Siberian crudes consist chiefly of relatively light paraffin hydrocarbons, a significant part of which is comprised of normal or slightly branched paraffins with high crystallization temperatures. In order to obtain the start of crystallization of the fuel below -60°C, the fractional composition of TS-1 is made lighter; TS-1 is light kerosene (see Fig. 12).

Fuels TS-1 and T-1 (particularly T-1) have an insufficient thermal stability. For this reason, new thermally stable fuel of grade T-7 has been introduced. It is produced from the same petroleum cut as TS-1 by hydrofining (refining with hydrogen) to remove unstable and corrosive impurities. At the same time, however, the antiwear properties of the fuel decline, and the tendency of combustion chambers toward gas corrosion increases (probably, under the influence of microimpurities, whose source is the metal catalyst during hydrofining).

The RT standardized fuel grade is designed for subsonic jet engines and supersonic engines of limited flight duration. It can be obtained from various crudes and by different processes - straight-run distillation using the hydrofining process and mixing of straight-run and hydrofined components. In fractional composition standards, RT fuel corresponds to aviation kerosenes of grade T-1 as well as grades TS-1 and T-7. In norms of content of mercaptan and total sulfur, actual gum and unsaturated hydrocarbons, and in thermal stability, acidity and calorific value, it corresponds to the best of the indicated grades, i.e., T-7 fuel. Its content of aromatic hydrocarbons is slightly lower than that of previous grades of aviation kerosenes, and control of flame emission has been provided for. The density of RT fuel has been established at not below 0.775 at 20°C (as in the case of TS-1 and T-7 grades), but if required by the consumer, RT fuel can be furnished with a density not below 0.800 with a simultaneous decrease in calorific value to 10,250 kcal/kg (as in grade T-1) and an inferior flame emission index [35, 60, 66, 72].

Wide-Cut Fuel

In contrast to T-1, TS-1 and T-7 fuels, which are aviation kerosenes, T-2 fuel has a wide fractional composition - it is a mixture of kerosene and gasoline.

When necessary, an increase in its production may ensure a significant increase in the yield of jet fuel from petroleum. T-2 fuel can be produced from low sulfur as well as sulfur crudes. In comparison with kerosenes, T-2 fuel has lower density (not below 0.755 at 20°C) and viscosity, inferior antiwear properties, and a higher saturated vapor pressure promoting cavitation in the airplane fuel system; in corrosive properties, it is usually no different from TS-1 fuel. Because of the disadvantages of T-2 fuel, the latter is not used in all types of engines, and reduced service periods of fuel pumps are established when it is used in a number of engines. For airplanes without fuel tank pressurization, the flight altitude is limited, during operation on T-2 fuel in the case of high fuel temperature in hot weather. [35, 60, 65].

Fuels with Additives

The thermal stability and antiwear properties of jet fuels have been improved by the development of special additives TP, P and others, which are introduced into the fuels during their production; the corresponding fuel grades with additives are designated TS-1TP, T-2TP, T-7TP and TS-1P, T-2P, T-7P. In antiwear properties, the wide-cut fuels T-2TP and T-2P are not inferior to aviation kerosenes and do not require a reduction of the working time of the fuel pumps and engines (the service life is read off hour after hour).

Mixing of jet fuels of different grades in tanks and preparation units is not allowed, since this would interfere with the verification of fuel quality; it could not be established what fuel grade norms the mixture should meet. In refueling airplanes, any grades allowed for use in a given type of airplane can be mixed in the fuel tanks [60, 109].

Heavy Kerosenes

For supersonic aircraft, hydrogenerated T-6 fuel of heavy fractional composition has been provided (see Fig. 12). Its density at 20°C is not less than 0.840. The high temperature of the start of boiling (not below 195°C) and removal of unstable and corrosive substances from this fuel should provide for normal operation of the aircraft fuel system and engines during prolonged supersonic flight under altitude conditions where the fuel is heated to 100-150°C or higher. T-5 fuel, which is close in fractional composition and has a density of not less than 0.845 at 20°C, not subjected to hydrofining, is markedly inferior to T-6 fuel in thermal stability; this fuel is suitable only for short flights. The high viscosity of T-6 and T-5 fuels at negative temperatures does not permit their use in engines whose fuel equipment is designed for ordinary kerosenes and wide-cut fuel (see Fig. 15). [58, 66].

Foreign Grades

Of the jet fuel grades used abroad, the most important are:

a) wide-cut fuel JP-4, or grade B (US brand), or AVTAG (British brand), or Air 3407 (French brand) with a density of 0.746-0.797 at 20°C, a saturated vapor pressure of 103-160 Torr at 38°C, and a freezing temperature around -60°C (it contains more gasoline fractions than Soviet T-2 fuel, and can be used only when it actually meets the norms of T-2 in aircraft where the latter fuel is allowed, including a saturated vapor pressure no higher than 100 Torr);

b) aviation kerosene Jet A and AI (US brand) or AVTUR/40, ATF-650 and AVTUR/50, ATF-750, ATK (British brands), or Air 3405 (French brand) with a density of 0.770-0.825, flash point of 43°C, and freezing points of -40 and -50°C respectively (can replace T-1, TS-1, T-7, with the exception of regions of lower temperature and prolonged high-altitude flights at subsonic speeds);

c) heavy aviation kerosene JP-5 (US brand) or AVCAT/40, AVCAT/50 (British brands) or Air 3404 (French brand) with a density of 0.783-0.841, flashpoint not below 60°C, and freezing temperature of -40 and -50°C respectively (can replace T-6 fuel when the norms for the latter are actually met).

Until recently, JP-4 fuel was the main grade in the US Air Force; from 1969-1970, its use was reduced (mainly because of its fire hazard) and a shift to kerosene type fuels was made. JP-5 fuel (of least fire hazard) is assigned mainly to naval aviation based on aircraft carriers.

In the last few years, thermally stable aviation kerosenes JP-6, JP-7, JP-8 have appeared in the USA for supersonic aircraft, having a higher temperature of the start of boiling and a lower temperature of the end of boiling in comparison with the other grades, and characterized by a better purification and the presence of additives [107, 110, 120].

EFFECT OF PROPERTIES OF THE FUEL ON ENGINE THRUST

Operating Characteristics Without Afterburning

As a rule, the properties of a fuel as well as its incomplete combustion have practically no effect on the magnitude of the thrust (power) of a gas

turbine engine, and hence, on the flying speed. At a high calorific value or high density, or in the presence of a better combustion efficiency, the regulator pump ensuring a given regulation program supplies a smaller volume of fuel. The fuel consumption under ordinary conditions ($\alpha > 1$) is established automatically so that the same amount of heat is evolved per unit time, the same thrust being thus obtained (other things being equal). The positive effect of a higher calorific value and density will affect the flight range and other factors dependent on the thrust impulse, but will not affect the thrust. However, the control devices of certain engines have structural characteristics that make them sensitive to the fuel properties. Thus, in VK-1 and RD-45F engines, the fuel density affects the maximum speed because their governor operates under the pressure of fuel thrown out by centrifugal forces during the rotation of the pump rotor (this pressure is proportional to the density). The maximum speed governor of these engines must be adjusted when changing from one fuel to another if the fuels have different densities.

In the AI-20 and NK-12 turboprop engines of various modifications, the automatic fuel control units dispense the fuel by volume. The fuel consumption per hour changes in proportion to the density, and so does the thrust of the engine according to the engine characteristic. When there is a considerable change in fuel density, it is necessary to readjust the gamma corrector present on the automatic fuel control unit of these engines [81].

Operating Characteristics with Afterburner

The thrust of turbojet engines with complete thrust augmentation, which is reached at the stoichiometric ratio of fuel to air ($\alpha = 1$) without "dilution"

of the combustion products with excess air, is almost independent of the composition and properties of the hydrocarbon fuels actually usable. This is due to the practically identical amount of fuel $\frac{H_u}{l_0} = 705 \text{ kcal } (\pm 1.5\%) \text{ per kg of air,}$ evolved by hydrocarbon fuels independently of their specific chemical composition (from which follows the approximate formula for the calorific value of hydrocarbon fuels $H_u \approx 705 l_0$). This is explained by the fact that fuels containing more hydrogen, and therefore evolving more heat, require correspondingly more air for their combustion. The same applies to ramjet engines operating at $\alpha = 1$.

In the operation of the afterburner pump of certain types of turbojet engines with afterburners at maximum operating efficiency, the amount of heat evolved, and hence, the engine thrust, is higher on fuels with a higher density or calorific value [81].

EFFECT OF FUEL PROPERTIES ON THE FLIGHT RANGE OF AN AIRCRAFT AND THE REQUIRED AMOUNT OF FUEL FOR PROGRAMMED FLIGHT

Calorific Power of a Fuel

The maximum quantity of heat that can be obtained during flight from the combustion of a fuel is equal to the product of the volume of the tanks by the density of the fuel and its calorific value $V_f \rho_f H_u$. In this expression, the product $H_u [\text{kcal/kg}] \rho_f [\text{kg/l}] = Q_u [\text{kcal/l}]$ represents the volume calorific value or energy capacity of the fuel, i.e., the amount of heat evolved by the combustion of 1 l of fuel. It is essential in determining the tank capacity when designing an aircraft.

The highest energy capacity is that of heavy kerosenes (T-6) followed by ordinary and light kerosenes (T-1, TS-1, T-7); the lowest calorific power is that of wide-

cut fuels (T-2) and gasolines (Table 7). This is due to the fact that as the fractional compositions of ordinary petroleum fuels becomes heavier, the density usually increases more sharply than the calorific value decreases. A similar effect is produced by increasing the content of aromatic hydrocarbons: their density is 10-15% higher than that of hydrocarbons of other groups and their calorific value is 4-6% less. Since the density of fuel changes with temperature (by approximately 1% for every 10°C, the energy capacity of fuels depends on their temperature [107]).

1. Наименование топлива	2. Теплота сгорания, ккал/кг	3. Плотность при 20° С	4. Энергоемкость (ккал/л) при различной температуре топлива, °С				
			+40	5 +20 (стандартная)	0	-20	-40
T-6	10350	0,840	8540	8680	8830	8980	9110
T-1	10250	0,820	8260	8420	8570	8720	8860
6. TC-1, T-7	10300	0,780	7850	8030	8200	8350	8500
T-2	10350	0,760	7690	7860	8000	8160	8330
7. Бензин Б-70	10400	0,730	7400	7590	7760	7940	8100

Table 7. Energy capacity (heat of combustion per unit volume) of fuels for gas turbine engines and of gasoline according to average factual data. Key:

1. Fuel; 2. Heat of combustion, kcal/kg; 3. Density at 20°C; -4. Energy capacity (kcal/l) at different fuel temperatures, °C; 5. +20 (standard); 6. TS-1; 7. B-70 gasoline

Nonequivalence of Calorific Value and Density

In operating airplanes, one must not assume that the flight range is proportional to the energy capacity of the fuel, and give preference to fuels of high density without considering their lower calorific value.

The effect of calorific value and fuel density on the flight range is not equivalent. The calorific value of a fuel always affects the flight range of an

aircraft, while the density does not always do so. In cases where the flight range depends on the fuel density, it is not proportional to the density. This is due to the fact that increasing the on-board fuel capacity by increasing the fuel density causes an increase in the flying weight of an aircraft and hence, an increased fuel consumption (in other words, part of the increased fuel capacity is consumed in the transport of the fuel). If however the flight takes place with the same initial flying weight, the increase in fuel weight due to its increase in density is associated with a corresponding decrease in payload. Finally, the amount of fuel required for a flight of a certain range (according to a specified program) is completely independent of its density; however, the calorific value affects both the amount of fuel and the size of the payload [73, 76].

Effect of the Flight Range

A key to the analysis of this question is the equation of impulses, according to which the flight range and other characteristics are proportional to the available fuel impulse $I_f = I_f \ln T$. It follows from Eqs. (1.11) and (1.12) that for two fuels with calorific values H_1 and H_2 , the ratio of available impulses

$$\frac{I_{f2}}{I_{f1}} = \frac{H_2 \ln T_2}{H_1 \ln T_1} \quad (3.1)$$

Of practical interest are three typical cases.

Case 1. The weight of the fuel is given ($G_f = \text{const}$). The fuel tanks are not filled completely, since the load taken requires a limitation of the fuel weight. Since $G_{f1} = G_{f2}$, $T_1 = T_2$ and hence,

$$\frac{I_{f2}}{I_{f1}} = \frac{H_2}{H_1} \quad , \quad (3.2)$$

i.e., the flight range is independent of fuel density and proportional to the calorific value of the fuel (more accurately, to the amount of heat evolved by the combustion of 1 kg of fuel). Wide-fraction fuel (of type T-2, which has a lower density but a slightly higher calorific value per unit weight and a higher combustion efficiency than T-1, provides a somewhat longer flight range in this case (by 1-2%). A range approximately 1% greater may also be expected from the combustion of T-7 and T-6 fuels.

Case 2. The payload is given ($G_p = \text{const}$). The fuel tanks of the aircraft are completely filled, and the payload $G_{p1} = G_{p2}$ is taken in such proportion that the initial flying weight of the aircraft does not exceed the allowed norm. According to Eqs. (3.1) and (1.14).

$$\frac{J_{f2}}{J_{f1}} = \frac{H_2 \left(n + 1 + \frac{V_f}{G_0 + G_p} p_{f2} \right)}{H_1 \left(n + 1 + \frac{V_f}{G_0 + G_p} p_{f1} \right)} \quad (3.3)$$

the flight range is proportional to the calorific value of the fuel and is related to density by a logarithm (weaker) dependence (Fig. 18). The available fuel impulse and flight range proportional to it change less with density than the initial weight of fuel aboard the aircraft, as a result of the dependence of the initial flying weight of the aircraft on the fuel density: $G_1 = G_0 + G_p + V_f \rho_f$. Thus, increasing the density by 5% from 0.800 to 0.840 gives only a 2.7% increase in impulse for a relative tank capacity of 1 l/kg, and a 4% increase for a relative tank capacity of 2 l/kg. When the density is decreased by 5% from 0.800 to 0.760, the impulse decreases by 3-4%.

Case 3. The initial flying weight is given ($G_1 = \text{const}$). The fuel tanks of the aircraft are completely filled, and the equality $G_{i1} = G_{i2}$ is achieved by correcting the payload as the density and weight of the fuel change. According to Eqs. (3.1) and (1.13) in this case

$$\frac{I_{T2}}{I_{T1}} = \frac{H_2 \ln \frac{1}{1 - \frac{V_f}{G_1} p_{f2}}}{H_1 \ln \frac{1}{\frac{V_f}{G_1} p_{f2}}} \quad (3.4)$$

As in the preceding cases, the flight range is proportional to the calorific value of the fuel, but its logarithmic dependence on density is more pronounced (Fig. 18). A 5% density change causes a 6.5-8% change in impulse provided $G_1 = \text{const}$. However, in this case, an increase in on-board fuel capacity due to an increase in density takes place at the expense of the payload: $-\Delta G_p = V_f \Delta \rho_f$. For this reason, the role of density is practically important only when the flight is carried out to maximum range with a limited payload [76, 81].

Required Fuel Capacity

When flights are carried out along a given route with a given profile, the most suitable fuel is one of high calorific value, since its required weight is smaller. At the same time, the fuel density does not play any part provided that the capacity of the tanks is sufficient for its accommodation. Flights according to the same program involve the same consumption of impulse and hence, the equality $I_{f2} = I_{f1}$, expressed according to Eq. (3.1) as $H_2 \ln T_2 = H_1 \ln T_1$, or

$$\frac{G_{i2}}{G_{i2} - G_{f2}} = \left(\frac{G_{i1}}{G_{i1} - G_{f1}} \right)^{\frac{H_1}{H_2}} \quad (3.5)$$

In the most typical case, in the transportation of the same payload ($G_{p1} = G_{p2}$) over a given distance, transformation of (3.5) yields the following dependence of the required quantity of fuel G_{f2} on its calorific value H_2 (in relation to a standard fuel whose weight is G_{f1} and whose calorific value is H_1):

$$\frac{G_{T2}}{G_{T1}} = \frac{1 - \xi_{T1}}{\xi_{T1}} \left[\frac{1}{(1 - \xi_{T1})^{\frac{H_1}{H_2}} - 1} \right] =$$

$$= \frac{1}{\xi_{T1}} \left[1 - (1 - \xi_{T1})^{\frac{H_1}{H_2}} \right] (1 - \xi_{T1})^1 - \frac{H_1}{H_2}$$

(3.6)

where $\xi_{f1} = \frac{G_{f1}}{G_{t1}}$ is the weight fraction of the first (standard) fuel.

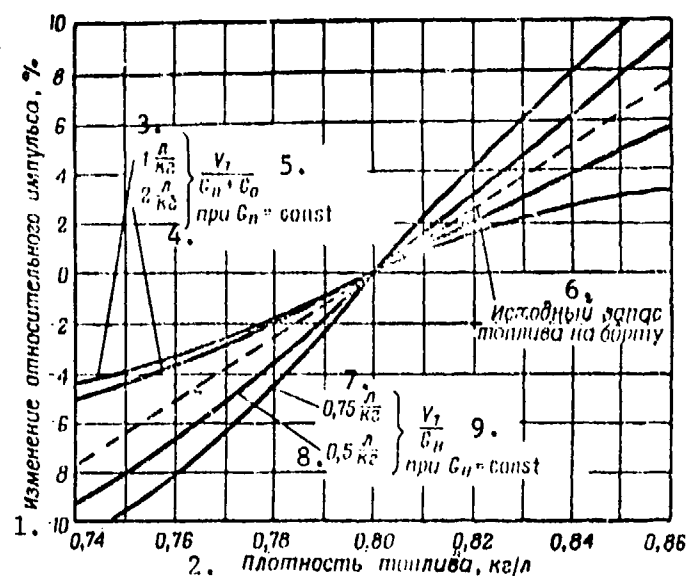


Fig. 13. Effect of fuel density on maximum flight range of aircraft for the same initial flying weight (line $G_1 = \text{const}$) or payload (line $G_p = \text{const}$); the range at fuel density $\rho = 0.8 \text{ kg/l}$ is taken as 100%.

Caption for Fig. 18

Fig. 18. Effect of fuel density on maximum flight range of aircraft for the same initial flying weight (line $G_1 = \text{const}$) or payload (line $G_p = \text{const}$); the range at fuel density $= 0.8 \text{ kg/l}$ is taken as 100%. Key:

1. Change of relative impulse, %; 2. Fuel density, kg/l ; 3. 1 l/kg ; 4. 2 l/kg ;
5. $\frac{V_f}{G_p} + C_0$ at $G_p = \text{const}$; 6. Initial on-board fuel capacity; 7. 0.75 l/kg
8. 0.5 l/kg ; 9. $\frac{V_f}{G_1}$ at $G_1 \text{ const}$.

When $G_p \text{ const}$, the required amount of fuel changes more sharply than the calorific value (Fig. 19): by 1.5-2% when the calorific value changes by 1% in the case of $\xi_f = 0.5$ to 0.75 . This is due to the change in initial flying weight corresponding to the change in the required amount of fuel.

If the initial flying weight is kept constant ($G_{i2} = G_{i1}$), and the payload is corrected, the influence of calorific value on the required on-board fuel capacity will of course be less pronounced. The corresponding transformation of relation (3.5) in this case gives the dependence:

$$\frac{G_{f2}}{G_{f1}} = \frac{1}{\xi_{f1}} \left[1 - (1 - \xi_{f1})^{\frac{H_1}{H_2}} \right]. \quad (3.7)$$

Knowing the initial flying weight, one can determine the gain or loss of payload thus obtainable:

$$\Delta G_p = G_{f1} \left(\frac{G_{f2}}{G_{f1}} - 1 \right) = G_1 \xi_{f1} \left(\frac{G_{f2}}{G_{f1}} - 1 \right). \quad (3.8)$$

Provided $G_1 = \text{const}$ a 1% increase in calorific value yields a fuel economy of only 0.5-0.7% when $\xi_f = 0.5$ to 0.75 (Fig. 19), but at the same time, a payload

gain of 0.3-0.5% of the initial flying weight is obtained, which for a heavy aircraft is significant. Approximately the same gain is obtained by decreasing the calorific value by 1%.

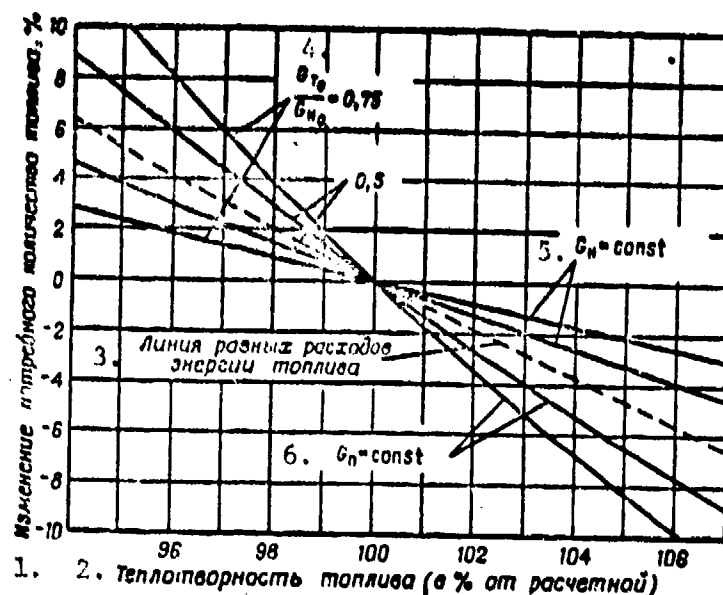


Fig. 19. Effect of calorific value (and factors on which the efficiency depends) on the required amount of fuel for flight over the same distance for the same initial flying weight (lines $G_i = \text{const}$) or payload (lines $G_p = \text{const}$); 100% of the required amount of fuel corresponds to any calorific value taken as 100%. Key:

1. Change in the required amount of fuel, %;
2. Calorific value of fuel (in % of calculated value)
3. Line of equal fuel energy consumptions.
4. $\frac{G_{f0}}{G_{i0}} = 0.75$; 5. $G_i = \text{const}$; 6. $G_p = \text{const}$.

Thus, in the case of a flight with a given (nonmaximum) range or limitation of fuel weight, it is not necessary to try to use scarce heavy aviation kerosenes; it is better to use readily available fuels of lower density and higher calorific value [76, 81].

Effect of Fuel Temperature

The available fuel impulse and flight characteristics dependent on it are sometimes also affected by other factors related to the fuel. Thus, at a high temperature of the wide-fraction fuel, its evaporation loss through fuel tank vents may reach several percent of the weight of the fuel, causing a corresponding reduction of the range or worsening other flight characteristics. At the same time, a decrease in fuel temperature, desirable from the standpoint of increasing the weight of the fuel charge and decreasing the evaporation loss, will cause a marked increase in viscosity, leading to a poorer mixing and reduction in fuel combustion efficiency. In the final analysis, the flight range will be decreased instead of increased. This may obviously occur in winter in cold regions, when T-1 fuel and heavier T-6 type fuels are used, since their viscosity-temperature characteristic is steeper than that of TS-1, T-7, and wide-cut fuels (see Fig. 15).

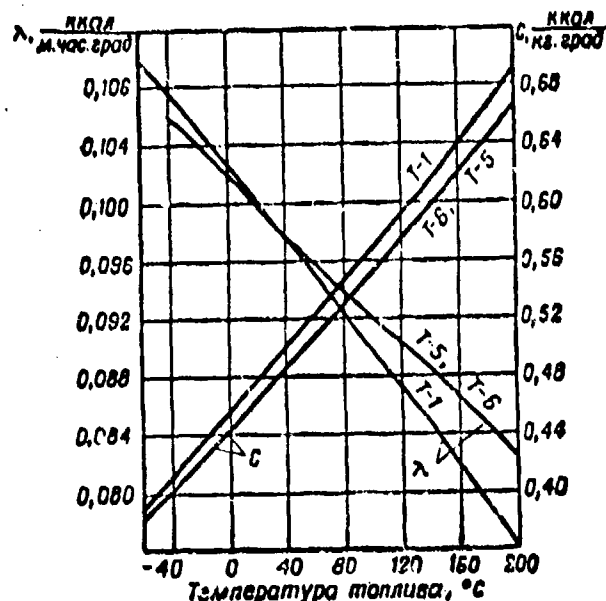


Fig. 20. Temperature dependence of thermal conductivity λ and heat capacity C of jet fuels. Key:

1. λ , kcal/m hr deg; 2. C kcal/kg deg;
3. Fuel temperature, °C

At a high supersonic flight velocity, a positive correction should be applied to the calorific values for the amount of heat transferred to the fuel as a result of its heating-up in the aircraft fuel system, $\Delta q = C_2 t_2 - C_1 t_1$ (the heat capacity C and temperature t with subscript 2 pertain to the fuel at the entrance to the engine, and with subscript 1, during refueling of the aircraft; the temperature dependence of the heat capacity is shown in Fig. 20). [14, 26, 81].

EFFECT OF FUEL PROPERTIES ON THE PERFORMANCE AND OPERATIONAL RELIABILITY OF THE FUEL SYSTEM OF AIRCRAFT AND ENGINE

Factors Causing Malfunctions

Breakdowns and failures in the operation of the fuel system of an aircraft and engine, related to the composition and properties of the fuel, may be caused by cavitation, difficulties in starting the engine (especially in flight), formation of ice crystals in the fuel, contamination and corrosion of the fuel equipment, and frictional wear of the friction surfaces of fuel pumps. Some of these effects are due to the heating up of the fuel during supersonic flight: the fuel temperature in the tanks reaches approximately 70°C after 3 hours, and in the course of delivery to the injectors, rises by an additional 50°C (and when the airplane lowers its altitude, by more than 100°C) in the heat exchangers and fuel equipment of turbojet engines [60, 73, 80].

Cavitation in the Fuel System

As the altitude increases, cavitation may occur in the aircraft fuel system, i.e., gaps and vapor-gas lock in the flow of liquid fuel, pressure fluctuations, and feeding interruptions. The phenomenon of cavitation is due to the solubility

of air and gases in the fuel and to the saturated vapor pressure of the fuel. The volume of air dissolved in the fuel is independent of the air pressure and usually amounts to 12-16% of the fuel volume. The weight of the air dissolved in the fuel is proportional to its pressure above the fuel (Henry's Law). Therefore, as the altitude increases, the weight of air dissolved in the fuel decreases in proportion to the pressure drop in the fuel tanks; the excess air separates out in the form of bubbles. The volume of air evolved is rather large (Fig. 21), and may reach several hundred liters for every 1000 l of fuel (if the expansion of air due to decreasing pressure with height is considered).

The volume element of air evolved $dV = \frac{dp_H}{P_H} V_d$ (where V_d is the volume of dissolved air). As the pressure gradually decreases from p_0 to p_H , the total volume evolved (which increases with increasing altitude)

$$V_{\text{cont}} = - \int_0^H \frac{dp_H}{P_H} V_d = V_d \ln \frac{p_0}{p_H}. \quad (3.9)$$

As a rule, the evolution of excess air from the fuel with increasing height has a lag, particularly at a high rate of climb. At a certain altitude (usually, not below 8000 m), this leads to a brief boiling up of the fuel. In this case, the following volume is simultaneously evolved:

$$V_{\text{sim}} = V_d \left(\frac{p_0}{p_H} - 1 \right). \quad (3.10)$$

The brief cavitation which then takes place in the lines and which causes a fluctuation of the fuel pressure presents no practical danger, provided that it does not cause any incorrect actions on the part of the crew.

Fuel evaporates into the air bubbles evolved. When during the climb the external pressure drops until it becomes equal to or lower than the saturated

vapor pressure, the fuel evaporation into the bubbles becomes very rapid, the bubbles expand markedly, and boiling begins. In certain parts of the aircraft fuel system, the pressure may be lower than the outside pressure (for example, at the entrance to the booster and transfer pumps). For this reason, cavitation of fuel in these sections of the lines begins at a lower altitude than the boiling of fuel in the tanks. During cavitation, the compressed mixture of liquid with fuel gases and vapors keeps moving along the lines. In this mixture, sharp pressure fluctuations arise readily, causing wear of the pump and fluctuations and interruptions in fuel consumption, up to and including interruption of the fuel supply.

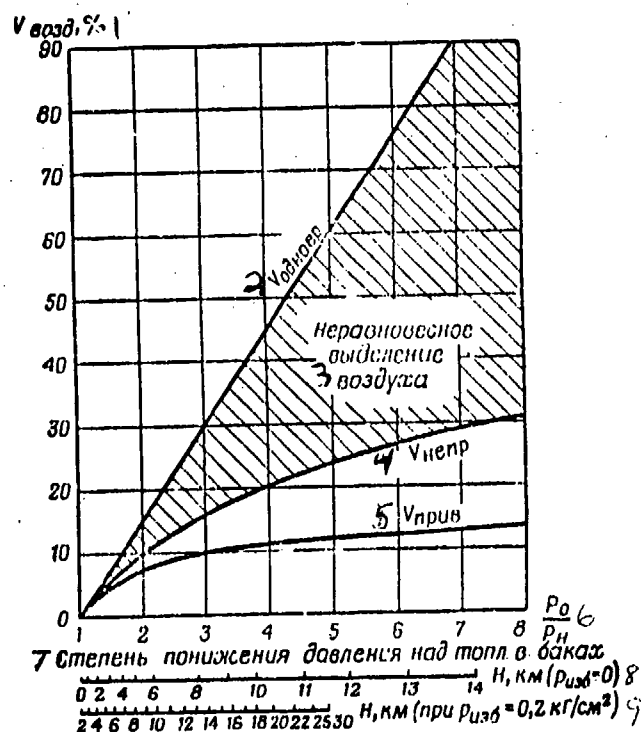


Fig. 21. Volume of air (in % of fuel volume) evolved by the fuel in the course of climb (if the solubility of air in the fuel is 15% by volume): V_{red} - volume of air reduced to standard pressure, 760 Torr, V_{cont} - during continuous evolution of excess air after climb.

Caption for Fig. 21.

Fig. 21. Volume of air (in % of fuel volume) evolved by the fuel in the course of climb (if the solubility of air in the fuel is 15% by volume): V_{red} - volume of air reduced to standard pressure, 760 Torr, V_{cont} - during continuous evolution of excess air in the course of climb, V_{sim} - during simultaneous evolution of all excess air after climb. Key:

1. V_{air} , %; 2. V_{sim} ; 3. Nonequilibrium evolution of air; 4. V_{cont} ;
5. V_{red} ; 6. $\frac{P_0}{P_1}$; 7. Degree of decrease of pressure above fuel in tanks;
8. H , km ($P_{exc} = 0$); 9. H , km (at $P_{exc} = 0.2 \text{ kg/cm}^2$)

Among fuels for jet engines, a saturated vapor (about 100 Torr and above) pressure dangerous from the standpoint of cavitation in the case of an open fuel system may occur in fuels of wide-cut composition in the summertime. Key measures against cavitation include the use of fuels with low vapor pressure, protection of fuel from heating by solar rays, installation of closed pressurized fuel systems, and raising the working pressure (cavitation margin) of booster and transfer pumps. Such steps are particularly necessary in the aircraft with high supersonic flying speeds, when heating of the fuel may cause a sharp rise in saturated vapor pressure (Fig. 22). However, excess pressure in the fuel system does not eliminate cavitation, but rather shifts it to higher altitudes and higher fuel temperatures (the two scales on the right of Fig. 22). As the fuel temperature in the tanks rises to 80-100°C, the high saturated vapor pressure makes it necessary to increase the strength and rigidity of the tanks. If the fuel tanks are filled with a nonreactive gas, the cavitation pattern does not change in principle, but the flight altitude at which cavitation takes place may shift to one or the other side. Thus, when carbon dioxide, whose solubility in the fuel is approximately three times as high as that of air, is used, the probability of cavitation at lower altitudes increases [35, 58, 81].

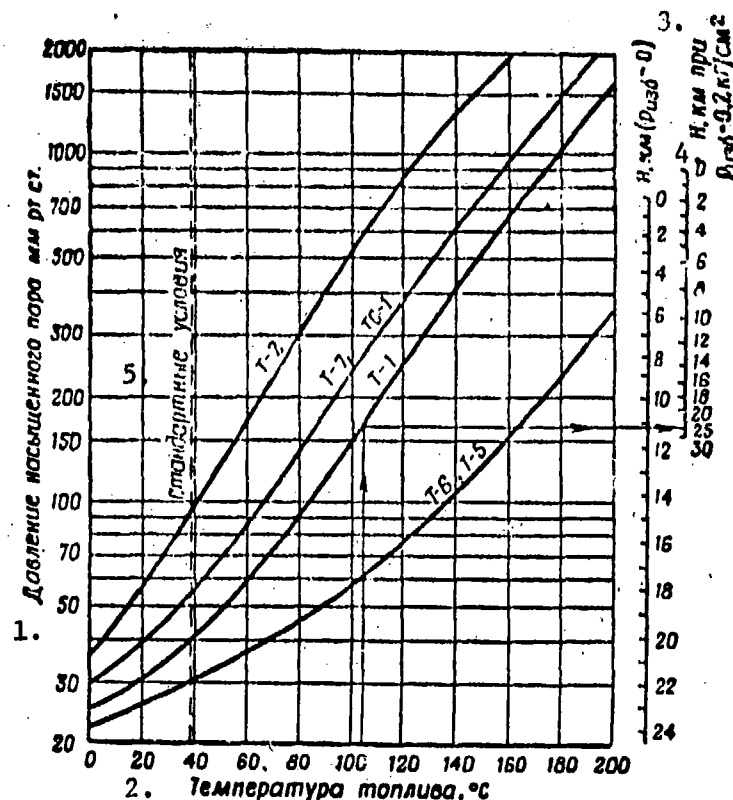


Fig. 22. Effect of fuel temperature on saturated vapor pressure; the flight altitude at which fuel boils in the presence of open draining of tanks ($p_{exc} = 0$) and of fuel tank pressurization ($p_{exc} = 0.2 \text{ kg.cm}^2$) is indicated on the right. Key:

1. Saturated vapor pressure, Torr; 2. Fuel temperature, °C; 3. H, km ($p_{exc} = 0$); 4. H, km at $p_{exc} = 0.2 \text{ kg.cm}^2$; 5. Standard conditions.

Engine Starting Difficulties

In order for an engine to start in flight it is necessary, first, that the electric discharge ignite the fuel in the starter, and second, that the arrival of hot gases from the starter to the return flow of air directed toward the injector (see Fig. 16) cause heating, evaporation and ignition of the working fuel. The first requirement is met by improving the design of starters and using starting fuels with a high saturated vapor pressure (nonethylated gasolines). At great altitudes (of the order of 12,000-15,000 m or higher, however,

the second requirement is not met: combustion of ordinary starting fuel is sluggish and yields so little heat that the latter cannot kindle the working fuel. For this reason, starters are equipped with oxygen feeding, and prior to starting in flight, the aircraft is lowered to the altitude at which starting is guaranteed. [2, 87, 112].

Ice Crystals

Under winter conditions of operation of aviation equipment, at a fuel temperature below 0°C (and during extended high-altitude flights in summer), ice crystals may form in the fuel. They clog the fuel filter of the engine before the pump and sharply decrease its transmissive capacity, causing engine shutdown. The appearance of ice crystals in the fuel may be due to three main causes: penetration of frost, condensation of moisture from air, and separation of water dissolved in the fuel.

When a reservoir, tanker, or aircraft fuel tank is being filled, frost that has settled on their walls may fall into the fuel. In addition, the frost formed on the walls of the container above the fuel level descends into the fuel when the container is heated by solar rays.

From the air entering the container through breathing valves or a vent, water vapor may condense on the surface of the cold fuel; this takes place when warm weather sets in. The condensation lasts one to two hours, until the fuel temperature rises. The fine ice crystals (of snowflake type) thus formed slowly sink into the fuel, remaining in the latter for a long time in the suspended state (their density is almost equal to the density of the cold fuel).

A small amount of water is dissolved in the fuel; its solubility decreases with decreasing fuel temperature and external pressure. Thus, in T-1 fuel at temperatures from +10 to 0°C, up to 60-80 g of water per ton may dissolve, and at -20°C, 2-3 times less (Fig. 23). When the fuel cools, for example in cold weather during filling of ground tanks with warm fuel from underground reservoirs or in summer during subsonic flight at high altitude, the excess water separates out in the form of fine droplets which freeze at subzero temperatures. Aromatic hydrocarbons dissolve many times more water than hydrocarbons of other groups (this is also evident from Fig. 23). They are the chief source of formation of ice crystals as the fuel temperature is lowered.

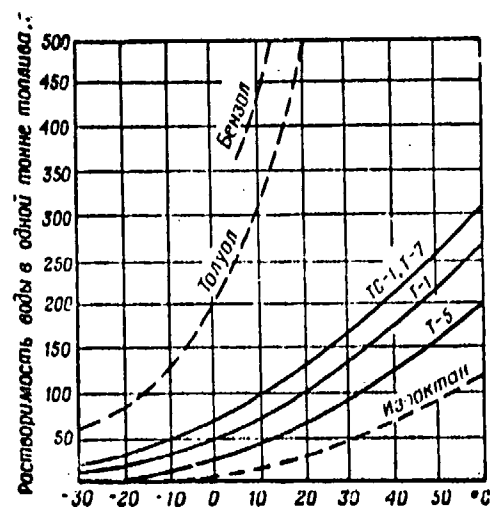


Fig. 23. Solubility of water in 1 ton at different fuel temperatures (air humidity being 100%) Key:

1. Solubility of water in 1 ton of fuel g;
2. Benzene;
3. Toluene;
4. TS-1;
5. Isooctane

The solubility of water in fuel is proportional to the water vapor pressure above the fuel, i.e., to the air humidity. With time (in several hours), an

equilibrium is established between the air humidity and the water content. The content of dissolved water in the fuel corresponds to the curves shown in Fig. 23 only at 100% air humidity (for example, at 20°C and at 100% humidity, 1 ton of T-1 fuel contains about 100 g of water). At a lower air humidity, a new equilibrium is gradually established (for example, in 1 ton of T-1 fuel at 20°C and at 40% air humidity, 40 g of water). If the air humidity is close to zero, the entire moisture gradually migrates into the atmosphere and is dispersed, so that there is no danger of crystal formation. However, if the air humidity exceeds 100% (rain, fog), the fuel not only becomes saturated with moisture, but also absorbs an excess amount of moisture (above the solubility limit), which separates in the form of ice crystals or as a precipitate on the bottom of the container. The higher the height of the fuel surface, the smaller the surface of its contact with air, and the higher the fuel viscosity, the more slowly equilibrium is reached.

It is evident from the above that special care must be taken when there are sharp fluctuations in fuel and air temperature. In winter, before filling the tanks with fuel, and also when the latter stays in aircraft tanks for a long time, it is necessary to check thoroughly for ice crystals in the fuel. The presence of ice crystals in aircraft tanks is detected during the preflight procedure and before taking off by draining and inspecting the fuel residue, and in certain types of aircraft, by inspecting the fuel filter after testing the engine [60, 79, 115].

Anti-icing Additives

An effective means of preventing the formation of ice crystals are anti-icing additives - ethylcellosolve and certain alcohols. They increase the

solubility of water in the fuel and keep it from precipitating out of solution when the fuel temperature falls. Ethylcellosolve is a colorless, transparent liquid with a slight ether odor; its density is 0.930-0.935 at 20°C. The alcohol-base liquid is colorless or slightly yellow with a pungent odor, and somewhat heavier, its density being 1.05-1.06 at 20°C. The permissible water content of both additives (before their addition to the fuel) is not above 0.5%. A water-containing additive must not be added, since it may introduce excess moisture into the fuel and cause the formation of crystals. Both additives are toxic: their vapors cause headache, and their presence in the digestive tract causes serious poisoning.

The anti-icing additive is added to the fuel in amounts of 0.1-0.3% (1-3 kg per ton of fuel) depending on the air temperature (on the earth's surface): 0.1% at temperatures down to -15°C; 0.2% at -15 to -25°C; 0.3% at temperatures below -25°C. In the dissolved state, the additive is capable of holding about 4% of water in relation to its weight, i.e., up to 120 g per ton of fuel when the content of the anti-icing additive is 0.3%. In practice, the amount of water in the fuel is always less than this value. Special dispensers are used for introducing the anti-icing additive. If ice crystals are present in the fuel, they dissolve upon addition of the anti-icing additive and after stirring for 20 to 30 min. When a water residue appears in the tank, the anti-icing additive passes from the fuel into the water, since the latter dissolves it better. Its content in the fuel is determined with a refractometer from the refractive index of light in a water extract prepared in a separatory funnel [1, 35, 115].

Residues and Corrosion in the Fuel System

The chief problem arising from the heating-up of fuel in flight is residue formation, which is most pronounced in the 130-200°C range (Fig. 24).

On hot surfaces (particularly bronze ones) in contact with liquid fuel, hard, scalelike deposits are formed, and in the fuel mass, a suspension of extremely fine solid particles which clog the filters and enter the channels and gaps of the fuel equipment. In the drainage holes, the sediment sometimes settles in the form of a loose mass. To prevent sedimentation, the fuel is purified as much as possible to remove sources of instability, i.e., hetero-organic compounds and unsaturated hydrocarbons, and an additive is introduced (for example, TP or P) in amounts of a few hundredths of one percent. Figure 25 shows the results of testing of the same fuel TS-1 with and without an additive, on a unit simulating a fuel system. However, very thorough purification of the fuel may decrease its stability by eliminating natural antioxidants (disulfides, phenols, etc.) [108].

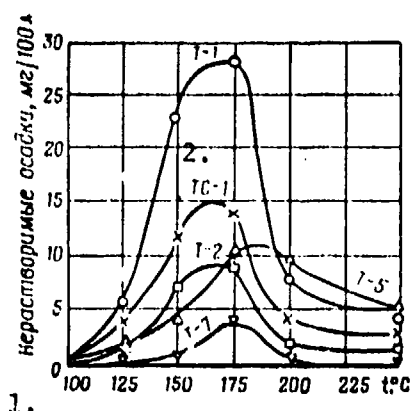


Fig. 24. Effect of temperature on the thermal stability of certain jet fuels
Key:

1. Insoluble residue, mg/100 ml; 2. TS-1

Contamination of fuel equipment with gelatinous corrosion products and gum, dangerous for control units, takes place in cases where the fuel contains an inadmissible quantity of mercaptan sulfur, organic acids, naphthenic soaps, and actual gum, which may result from lapses in fuel quality control.

In recent years, attention has been focused on still another form of corrosion, microbiological corrosion [93]. Petroleum products almost always contain bacteria and spores of molds, but they appear only under conditions of considerable humidity and relatively high fuel temperature. They multiply rapidly on the surface of contact between the fuel and water, on moist walls of aircraft fuel tanks, refueler, depot, etc. During their metabolism, they secrete acid organic matter, and possibly, hydrogen sulfide and sulfuric acid, which may cause serious damage, particularly in the course of prolonged action inside stagnant parts of the fuel system (even leakage of caisson tanks may result). In addition, a bacterial mass may contaminate the automatic controls and clog the filters.

The principal measures aimed at controlling microbiological corrosion include regular drainage and checking of the sediment, thorough washing of the systems (especially in tropical climates) and also the use of biocidal fuel additives. It is known that the anti-icing additive has a biocidal action [1, 35, 58, 60, 95, 107, 108, 123].

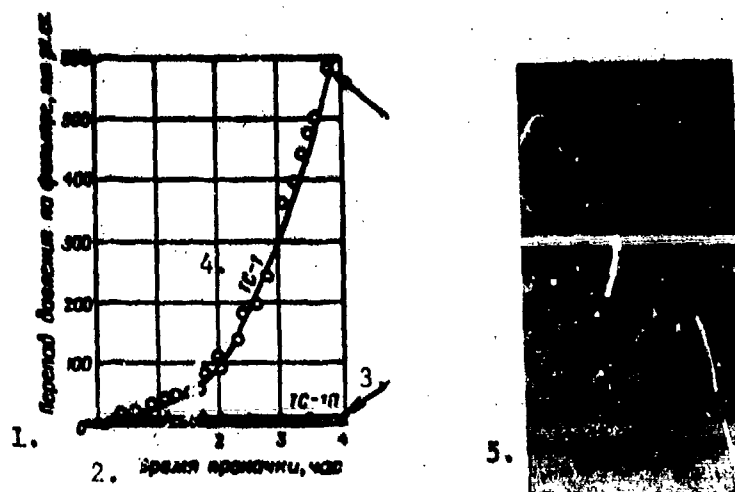


Fig. 25. Effect of an additive increasing the thermal stability of a fuel on the pumpability of the fuel (at 180°C) and condition of the filter after pumping. Key:

1. Pressure drop at filter, Torr; 2. Pumping time, hr;
3. TS-1P; 4. TS-1; 5. Photomicrograph of filter.

Friction Wear of Pumps

The antiwear properties of a fuel are chiefly determined by the surface activity, i.e., the ability of a fuel or any other substances present therein to be absorbed on a metal surface. This prevents "stripping" and dry friction of fuel pump parts in sections of high contact pressure forcing the fluid out of the gap. The highest surface activity is displayed by substances whose molecules are electric dipoles. The higher the dipole moment of the molecules, the stronger the "adhesion" to a surface whose electric field is not compensated. Fuel hydrocarbons have a small dipole moment and their antiwear properties are slight. Among substances which may be naturally present in petroleum fuel, those having large molecular dipole moments are resins, organic acids and other oxygen-containing compounds and organic sulfur and nitrogen compounds, i.e., substances whose presence is harmful from the standpoint of

thermal stability and corrosion properties. Thus, hydrofined fuel T-7 is inferior in antiwear properties to TS-1 fuel, which is made from the same stock. Apparently, there is an optimum content of heteroorganic compounds in the fuel which ensures lubrication of the pumps and is not dangerous from the standpoint of sedimentation.

A certain influence on the antiwear properties is also exerted by the fuel viscosity. The composition of less viscous fuels includes substances of lower molecular weight whose molecules are smaller in size, and hence, have a smaller dipole moment. For this reason, for the same degree of purification and in the absence of antiwear additives, the strength of the boundary film which they form on a metal surface is lower. In addition, as the molecules become smaller, the average velocity of their random thermal motion promoting the destruction (desorption) of the boundary film increases.

An appreciable improvement of the antiwear properties of jet fuels is achieved by introducing a few hundredths of one percent of a surfactant [109] whose molecules have a large dipole moment. Such additives are, in particular, the same TP and P which increase the thermal stability of fuels. T-2TP and T-2P fuels possess adequate antiwear properties and may be used in equipment where T-2 fuel of the same viscosity but without an additive does not provide for a reliable operation of the fuel pumps. Introduction of an additive into hydrofined T-7 fuel compensates decreases in antiwear properties caused by its "excessive refining."

A complex influence on the lubrication and wear of parts is exerted by oxygen dissolved in the fuel. By reacting with the fuel as the temperature is

raised, oxygen dissolved in the fuel. By reacting with the fuel as the temperature is raised, oxygen participates in the formation of heterorganic compounds useful for boundary lubrication, but by heating the metal in the zone of high contact loads, it promotes destruction of surfaces of the parts. Up to a fuel temperature of 90-100°C (by volume), reinforcement of the latter effect, which accelerates wear, prevails. At higher fuel temperatures, the wear decreases, apparently because of the formation of a large quantity of surface active substances throughout the volume of the fuel, including those that react chemically with the metal and produce an antifriction layer on its surface. It is also possible that as the temperature rises, a positive role is played by the decrease of solubility, and hence, of the oxygen concentration in the fuel. An artificial decrease of the content of dissolved oxygen in the fuel through treatment of the fuel with nitrogen substantially decreases the wear of pumps [1, 35, 49, 107, 108].

EFFECT OF FUEL PROPERTIES ON THE RELIABILITY OF THE PARTS OF THE ENGINE GAS CIRCUIT

Fuel has three types of effects on the gas circuit of an engine: thermal, contaminant (scale forming), and chemical (corrosion).

Thermal Radiation

The convective heat transfer of combustion products is practically independent of the properties of the fuel. However, the radiant heat transfer of a flame, not weakened by an obstructing layer of air, is determined by the sootiness of the flame and depends on the fuel composition (Fig. 26). The scale of luminometric numbers has been adopted abroad for estimating fuels according to

the radiation intensity of their flame. These numbers are determined on a luminometer, i.e., a diffusion flame equipped with instruments for measuring flame brightness and the temperature increment produced by the flame. The larger the temperature increment at the same brightness, the better is the fuel considered to be and the higher its luminometric number.

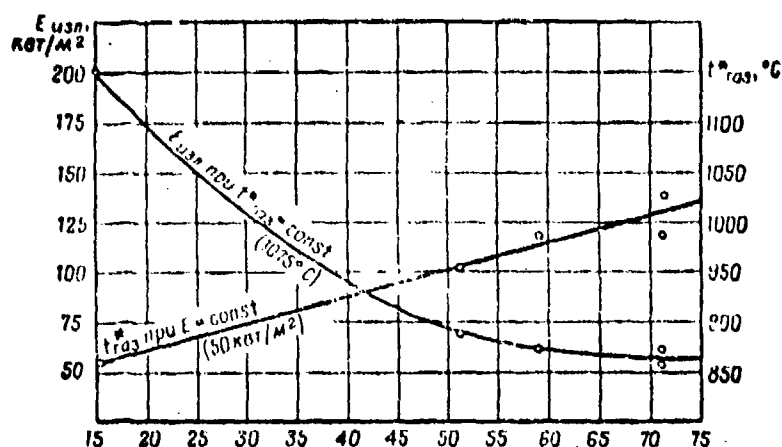


Fig. 26. Luminometric number of a fuel with radiated flame energy E_{rad} (at $t^*_{gas} = \text{const}$) versus gas temperature t^*_{gas} at the exit from a model combustion chamber (at $E_{rad} = \text{const}$). Key:

1. E_{rad} , kW/m^2 ; 2. t^*_{gas} , $^{\circ}\text{C}$; 3. E_{rad} at $t^*_{gas} = \text{const}$; 4. t^*_{gas} at $E = \text{const}$ (50 kW/m^2)

The highest luminometric numbers (above 100), i.e., a weak radiation, is exhibited by normal and slightly branched paraffins and naphthenes (isooctane or 2,2,4-trimethylpentane is taken as 100), and low luminometric numbers (below 20), i.e., strong radiation, characterizes aromatic, naphthenic-aromatic, and bicyclic aromatic hydrocarbons (tetralin, a bicyclic naphthenic aromatic hydrocarbon, is assigned the value zero). Highly branched isoparaffins and naphthenes and bicyclic naphthenes are located in the middle of the scale. The more "compact" the molecule, the higher the soot-forming tendency, the stronger the radiation, and the lower the luminometric number.

Data are available on the correspondence between the results of tests of fuels on a luminometer and in combustion chambers of turbojet engines: the higher the luminometric number, the weaker the thermal flux emitted by the flame and the lower the wall temperature of the fire tube. This is considered to be essential in ensuring the fatigue strength of thermally stressed combustion chambers. Modern jet fuels have luminometric numbers of 40-70. T-1 fuel is characterized by luminometric numbers of 50-55 (but some samples may have lower numbers), and TS-1 and T-7 fuels, by numbers of the order of 60-70. These numbers represent the "blending" rating of the hydrocarbons comprising the composition of the fuel; hydrocarbons with low luminometric numbers have a stronger influence on this blending index. At high flying speeds ($M > 3$), in view of the rise in flame temperature, it is assumed that fuels with luminometric numbers of about 100 will be required.

A disadvantage of the luminometric scale is its nonuniformity: fuels differing considerably in actual emission in engines are estimated in almost identical fashion in the lower part of the scale, whereas the upper part is of publicity value, i.e., huge increases of luminometric numbers correspond to practically insignificant changes of radiant flux under actual conditions. In this connection, it is suggested that instead of the luminometric number, use be made of the flame blackness index, which is inversely related to the luminometric number. This index is proportional to the concentration of soot in the flame and to the thermodynamic degree of blackness of the flame, usually employed in thermal calculations [94, 107, 123, 138].

Carbon Deposition

When the flame is close to the burner, a deposit forms near its nozzle, and the spraying of the fuel worsens, or its cone becomes distorted. As a result, liquid fuel falls on the fire tube walls and burns on them, causing overheating of the walls and a rapid formation of a deposit consisting mainly of carbonized residues of aromatic hydrocarbons, tars, etc. A significant content of aromatic hydrocarbons in this case promotes overheating, buckling, and burnout of the fire tube walls and other parts because not only of a more intense flame radiation, but also absorption by the black surface of the wall. Particles of the deposit which become detached from the fire tube walls strike the turbine blades and cause their premature wear (erosion).

A dense film of ash slag is formed after the combustion of microimpurities of metals present in the fuel in the form of salts and possibly in the composition of complex organometallic compounds. In the molten or softened state, metal oxides and salts stick to the parts, then solidify on cooling [34, 69, 106].

Gaseous Corrosion

The presence of vanadium pentoxide V_2O_5 and possibly other metals in fuel ash cause corrosion and burnout of iron- and nickel-base alloys which are oxidation-resistant at high temperatures.

A trace impurity of vanadium (0.00001-0.01%) enters into the composition of mainly high molecular nitrogen-containing compounds which concentrate in the high-petroleum fractions and are largely eliminated by refining of the petroleum

products. However, the negligibly small amount of remaining vanadium may apparently act as an oxygen carrier and catalyst of gaseous corrosion, and may be directly responsible for the corrosion and burnout of materials which are oxidation resistant at high temperatures. The vanadium pentoxide (melting point 685°C) formed after the combustion deposits in the gas circuit in the liquid state, and because of the variable valence of vanadium, changes into the tetroxide, $\text{V}_2\text{O}_5 \rightarrow \text{V}_2\text{O}_4 + \text{O}$; the atomic oxygen oxidizes iron or nickel. On contact with excess oxygen in the gas circuit, the tetroxide is converted back to the pentoxide, dissociates again, and so on. A slight content of sodium sulfate Na_2SO_4 or sodium oxide Na_2O in the fuel ash increases vanadium corrosion of iron by a factor of several dozen. The problem of vanadium and similar corrosion and steps aimed at controlling it has not been adequately solved. The prevention of this type of corrosion is accomplished by quality control testing of the fuels.

Prolonged corrosive action of sulfur dioxide formed during the combustion of sulfur compounds (in some fuels, SO_2 is present in fairly large quantities, up to 0.25%, in the form of inactive compounds) may cause burnout of turbine blades if their temperature is above $900\text{--}950^{\circ}\text{C}$ [35, 44, 50, 60, 81].

FIRE HAZARD OF FUELS

Self-Ignition

A fire may be caused by self-ignition of fuel or flareup of its vapors, ignited by an external source, i.e., a flame or electric spark. The process of self-ignition of hydrocarbon fuel takes place directly only in the vapor phase as a result of explosion of hydroperoxides formed when hot fuel vapor comes in

contact with oxygen. In practice, instantaneous formation and self-ignition of a fuel-air mixture take place when kerosene falls on a hot metal surface at temperatures above 350-400°C, for example, on the jet nozzle or parts of a turbine damaged by failure.

The self-ignition tendency of a fuel must not be confused with the possibility of ignition by an external flame. Heavier hydrocarbons self-ignite more easily; they oxidize more readily by nature, forming explosive peroxides - kerosenes approximately 100°C lower than gasolines. Still easier is the self-ignition of hydraulic oil, similar in hydrocarbon composition to diesel fuel, and lubricating oil falling on hot engine parts. In breakdowns and in cases of damage, they usually form the first flame centers which then ignite the fuel.

The danger of self-ignition is manifested under conditions of supersonic flight at large M numbers when the fuel vapor is heated in the tanks to 200°C or higher if oxygen is present in the tanks in the space above the fuel. For this reason, it is necessary to pressurize the fuel tanks with a neutral gas (for example, nitrogen). However, it must be kept in mind that as the aircraft climbs and the fuel heats up, air enriched with oxygen escapes from the fuel (oxygen dissolves in the fuel in larger quantity than nitrogen). This increases the danger of self-ignition of vapor inside the fuel tanks. A radical step eliminating the danger of self-ignition consists in first decreasing the oxygen concentration in the fuel by purging it with nitrogen [52].

Ignition by an External Source

Volatile fuels are more dangerous when exposed to external ignition sources such as careless handling of a flame, damage to electric wiring, or a discharge

of static electricity. Fuel is ignited by an external source only at a temperature above the flash point, when a mixture of fuel vapor and air sufficiently rich for ignition is formed above the fuel. Thus, vapors above T-1 fuel are explosive if the fuel temperature is not below 25-30°C; above TS-1 fuel, not below 15-25°C, and above T-2 fuel (containing gasoline), starting at a temperature of minus 10-20°C. At a lower temperature, fuels are not ignited by a spark or a brief presence of an external flame.

In theory, there also exists an upper temperature limit of fuel ignition (for T-1, about 65°C; for TS-1, 55-60°C; for T-2, 40-45°C) at which an extremely rich mixture incapable of igniting is formed above the fuel, and the lower and upper ignition limits come closer together as the pressure in the tanks decreases with increasing flight altitude. However, this is of no practical importance, since the probability of ignition of the fuel at a temperature above the theoretical upper limit is retained owing to the above-mentioned evolution of oxygen from the fuel as the aircraft climbs [78].

Ignition by Static Electricity

During the filling of fuel tanks and refuellers at a fast pouring rate, electrification of the fuel takes place as a result of friction against the material of the filters and hose walls. As a rule, the fuel acquires a positive charge (gives up electrons during friction). In dry weather, the voltage on the surface of the fuel in the tanks toward the end of the filling amounts to a thousand volts, which may cause a powerful spark discharge. This takes place as a result of accumulation of static electricity due to the low electrical conductivity of dry fuel. The charge of moist fuel (containing dissolved or

emulsified water) is several times smaller. If the fuel temperature during the filling of tanks, delivery into tank cars or refuelling of aircraft is above the explosive limit, the spark discharge of static electricity may cause a fire.

The problem of fuel electrification has become more serious as a result of measures aimed at increasing the thermal stability of fuels. Extensive purification of fuels involving removal of electrically polar heteroorganic compounds decreases the electrical conductivity of fuel, and some of the additives introduced to improve its thermal stability and lubricating properties enhance its electrification.

As a step designed to prevent the accumulation of static electricity, its discharge and the consequent fire hazard, one can recommend that the pouring rate of the last 20-25% of the fuel be decreased in the presence of low air humidity. In addition to the usual grounding of the aircraft and refueller, the filler nozzle should be connected by a wire to the tank filler. The electrical conductivity of the fuel can be increased and a rapid dispersal of the electrostatic charge can be achieved by introducing special additives into the fuel; it is well known that the antistatin additive is present in certain foreign fuels [107, 120].

PROSPECTIVE FUELS FOR JET ENGINES DESIGNED FOR HIGH SUPERSONIC FLYING SPEEDS¹

Basic Problems

As the flying speed increases to $M=3-4$ and above, the problems of ensuring the thermal stability of the fuel, using the fuel as a cooling agent in the

¹According to material given in the foreign press.

aircraft and increasing the energy characteristics of the fuel are considered to be increasingly acute. The following possible solutions of these problems are considered:

- a) radical improvement of petroleum fuels of kerosene type by extensive hydrogenation and use of polyfunctional additives;
- b) development of hydrocarbon fuels which absorb heat during chemical reactions in the heat exchanger of the aircraft;
- c) use of liquefied hydrocarbon gases including liquid natural gas;
- d) use of liquid hydrogen;
- e) use of nonhydrocarbon fuels for short-time jet engine thrust augmentation;
- f) use of nuclear energy [118, 119, 120, 123, 129, 132, 138, 141].

Improvement of Petroleum Fuels

The production of fuels via catalytic hydrocracking of heavy petroleum stock permits a substantial increase in thermal stability and decrease in corrosiveness and intensity of sooting and flame radiation, i.e., those properties which are considered decisive at $M=3-4$. It turns out to be possible owing to a significant yield of cheap commercial hydrogen as a by-product of a series of petrochemical processes. However, certain properties of the fuel decline as a result of hydrogenation. The content of surface active substances and natural antioxidants in the fuel decreases, causing a decrease in the lubricating properties of the fuel, and the thermal stability increases less than might be expected. These disadvantages may be offset by introducing additives; the latter may also provide for a further increase in thermal stability, produce an anticorrosive effect, etc. In particular, such additives are considered to be the copolymer of methacrylic acid esters, isopropyloctadecylamine $C_3H_7NHC_{18}H_{37}$.

A drawback of hydrogenated fuels is their low density (approximately at the level of TS-1 fuel); this may be compensated to some extent by a slightly higher calorific value due to maximum hydrogenation of the fuel and a lightening of the fractional composition. At the same time, a slight temperature rise of the start of crystallization of the fuel is possible [73, 107, 118, 123, 129, 138].

Fuels for Chemical Cooling

Heat-absorbing fuels are being suggested for use in chemical cooling of equipment and systems of prospective aircraft with number $M > 4$ (the temperature of brought-to-rest air in the stratosphere at $M=4$ is 625°C , and at $M=5$, about 1000°C). The most suitable reactions are considered to be endothermic reactions of cracking of paraffins and dehydrogenation of naphthenes, for example, methylcyclohexane C_7H_{14} (with platinum and aluminum oxide as catalysts) and decalin $\text{C}_{10}\text{H}_{18}$, providing for the absorption of 1080-1100 kcal/kg (along with vaporization). Thus, the heat exchangers of an aircraft should be converted into petrochemical reactors. In this case, the cooling process is a regenerative one, and the energy absorbed by the fuel enters the engine. However, it is necessary to solve a series of complex problems - preventing the formation of deposits in the reactor heat exchanger, and suitability for direct use in the engine of the conversion products of the original fuel [130, 132, 142].

Cryogenic Fuels

The use in supersonic aircraft of cryogenic fuels, i.e., liquid hydrocarbon gases and liquid hydrogen, makes it necessary to have thermal insulation

and to increase the weight and volume of the fuel system, and involves the loss of a part of the fuel. What qualities of cryogenic fuels make them promising? Primarily, their cold service life, which provides for an efficient cooling of the aircraft, and thermal stability (extremely high for methane and absolute for hydrogen), followed by high energy characteristics and desirable fire properties (high combustion rate, very low flame radiation). Natural gas, the bulk of which consists of methane, is much cheaper than present-day aviation fuels, and certainly much cheaper than prospective fuels. Hydrogen is relatively expensive, but its cost is decreasing each year.

Methane (CH_4) as fuel has the following basic properties: boiling point -161.5°C , density at this temperature, 0.424, heat of vaporization, 123 kcal/kg, freezing point, -182.5°C . The heat of formation of methane (gaseous) is 1110 kcal/kg. The calorific value of gaseous methane is 11,980 kcal/kg, and that of liquid methane 11,820 kcal/kg (14-15% above that of kerosene). The stoichiometric coefficient of methane with air is 17.23, and the maximum quantity of heat per 1 kg of air in terms of gaseous methane is 695 kcal/kg (1.5% less than that of kerosene). Liquid hydrogen as the combustible component of jet fuel is discussed in Ch. 5; its energy indices are given in Tables 3 and 5. In comparison with kerosene, the calorific value of liquid hydrogen is 2.7 times higher, and the maximum quantity of heat per 1 kg of air in terms of gaseous hydrogen is 835 kcal/kg (18% higher). The density of liquid hydrogen is 11-12 times lower than that of kerosene. Data on calorific value per unit weight show the desirability of using both fuels as "cruising" fuels, i.e., fuels with a lower specific consumption in comparison with kerosene during prolonged flights in the atmosphere [127, 141].

"Acceleration" Fuels

Liquid hydrogen may also be regarded as an "acceleration" fuel, which provides thrust augmentation at $\alpha = 1$ as a result of a large supply of heat per unit of air consumption in comparison with ordinary hydrocarbon fuels. Other compounds which can be used as acceleration fuels are the high-energy boron hydrides; pentaborane, decaborane ($H_u/l_0 \approx 1220$ kcal/kg of air), as well as certain low-energy fuels requiring a small amount of air for their combustion, i.e., with a low stoichiometric coefficient l_0 . The latter include nitrogen-containing fuels - dimethylhydrazine ($H_u/l_0 = 778$ kcal/kg of air), hydrazine ($H_u/l_0 = 920$ kcal/kg of air) and metals - magnesium, lithium, aluminum (H_u/l_0 respectively 2080, 2050, 1900 kcal/kg of air). Their effect is explained by an increase in fuel consumption such that the hydrocarbons are unable to burn. At the same time, the range in a steady flight regime decreases sharply; in a prolonged cruising flight in the atmosphere, acceleration fuels are less efficient than kerosene. However, thrust augmentation in the case of short-time use of such fuels, and also when used as additives to the main fuel, may provide a rapid acceleration of the aircraft [35, 73, 86, 103].

Nuclear Fuel

In both a gas turbine and a ramjet engine, air can be heated by using an atomic reactor or an associated radiator instead of an ordinary combustion chamber. The realization of these projects is prevented by the danger of contaminating the atmosphere with radioactive substances [47, 73, 119].

CHAPTER 4

AVIATION GASOLINES

CHARACTERISTICS OF PISTON ENGINES AND FUEL REQUIREMENTS

Description of the Work Process

Gasolines are fuels mainly for piston engines with spark ignition. The requirements placed on the quality of present-day grades of aviation gasolines are determined by the characteristics of precisely this category of engines. Gasoline grades most suitable for use in engines of other categories are selected from those designed for piston engines. A characteristic feature of the working process of piston engines is their cyclicity. It imposes severe limitations on the available carburation, ignition and combustion times (hundredths of a second). For this reason, the vaporizability of a fuel and its self-ignition knocking tendency play a decisive role in the realization of the thermodynamic cycle of piston engines and in ensuring their normal operation [11, 60, 81].

Vaporizability

In order to achieve combustion at constant volume, spark ignition engines require an easily vaporizable fuel - gasoline, since it makes it possible to obtain rapidly (before the spark) a homogeneous fuel-air mixture ready for combustion. A time of about 0.02 sec is allowed for carburation in the working cycle. The degree of vaporization of gasoline during this time interval substantially depends on its fractional composition and in turn affects the operational characteristics of the engine. Starting of a cold engine at low temperature

is easier the lower the temperature at which 10% of the fuel volume boils away (this fraction is called the starting fraction). Aviation gasolines have boiling temperature of the 10% fraction not above 75-88°C. The warmup time of the engine and its acceleration (time required to pass from idling to maximum operation) decrease with decreasing temperature of boiling of the 50% fraction of gasoline. To achieve the required acceleration time of 1-2 sec, it should be no higher than 105°C.

The degree of vaporization of gasoline and the uniformity of the composition of the mixture in the engine cylinders depend on the boiling temperature of the 90% fraction of gasoline. If this temperature is high (higher than approximately 145°C), part of the fuel descends from the pipe walls and enters certain cylinders of carburetor engines in the form of a liquid film. As a result, the engine fails to develop the required power, its economy drops, and the nonuniformity of the mixture composition causes shaking. The boiling temperature of the 97.5% fraction of gasoline (practically the end of boiling) also affects the engine economy, and in addition, the carbon deposition, the dilution of crankcase oil by unburned fuel residue, and in the final analysis, the degree of wear and service life of the engine. Experiment shows that this temperature should be no higher than 180°C.

To prevent gasoline from boiling in hot weather, the temperature of the start of its boiling should not be below 40°C. In order to avoid cavitation in flight, the saturated vapor pressure of gasoline (at 38°C) should not exceed 360 Torr. To facilitate the starting of aviation engines in winter, the lower limit of saturated vapor pressure is also standardized, namely, at 220-240 Torr [60, 81].

Antiknock Value

After the fuel-air mixture ignites, the flame propagates through the combustion chamber as a front in 0.002-0.003 sec. On expanding, the combustion products sharply compress, and hence, strongly heat up the still-unburned mixture ahead of the flame front. As a result, rapid oxidation of hydrocarbons take place in this mixture, and easily exploding hydroperoxides are formed. If the peroxides are unable to form and explode before the end of combustion of the mixture, the engine will operate normally, but if the explosion of the peroxides is ahead of the normal combustion front, shock waves are formed in the cylinder and knocking takes place, with a marked heat transfer to the walls. This causes overheating and a gradual destruction of parts of the cylinder-piston group.

The rate of formation of hydroperoxides and correspondingly, the possibility of knocking are determined by the hydrocarbon composition of gasoline. A high antiknock value characterizes isoparaffins (it is lower the more branched the carbon skeleton of their molecules) and many naphthenes and aromatic hydrocarbons (the latter when the engine operates on a rich mixture, $\alpha = 0.6-0.8$). A low antiknock value characterizes normal paraffins, particularly with a long chain of carbon atoms in the molecule. The addition of the antiknock compound tetraethyllead (in amounts of the order of 0.3%) substantially increases the antiknock value of gasoline. This compound slows down the process of formation of explosive hydroperoxides.

The occurrence of knocking depends on the regime and operating conditions of the engine: boost pressure p_c , whose change regulates the power of the aircraft piston engine, excess air ration α , temperature t of air forced into the

cylinders, and temperature t_{cy} of the engine cylinders, the influence of these factors being intertwined. The most complete representation of this influence is provided by the knocking characteristics, i.e., the dependence of the maximum permissible boost pressure \bar{p}_c (corresponding to the start of knocking) on the composition α of the mixture at different temperatures t_c and t_{cy} (Fig. 27). At high air temperatures (above 100°C , the usual value of t_k in summer and winter after compression in the supercharger) and a high temperature of the cylinders t_{cy} , the maximum antiknock value (maximum \bar{p}_c) is obtained at $\alpha = 0.6-0.7$ (rich mixture), and the minimum at $\alpha = 1.0-1.1$ (lean mixture). When the engine operates on a rich mixture, this makes it possible to establish a higher boost and to obtain greater power from the engine than in operation on a lean mixture. Decreasing the temperature regime to t_c and t_{cy} values corresponding to the winter conditions of engine operation causes a decrease in the antiknock value on a rich mixture and an increase on a lean mixture. In other words, at the maximum cruise power setting, knocking is more probable at a low air temperature, and at the cruise power setting, at a high air temperature.

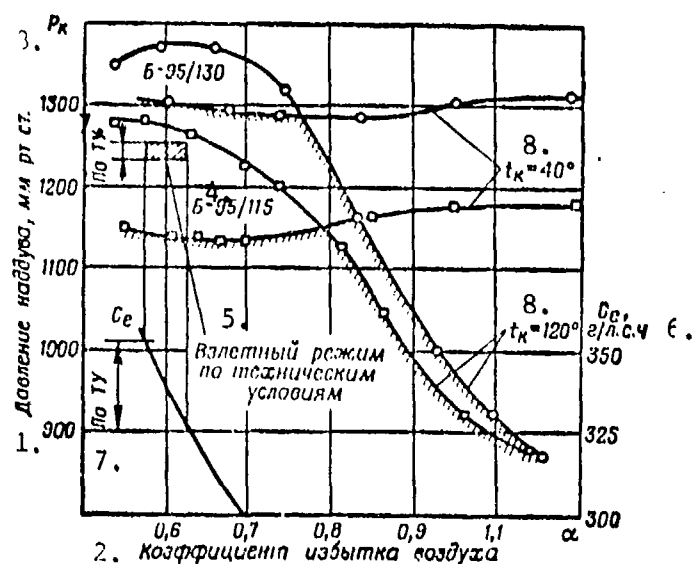


Fig. 27. Knocking characteristics of gasolines in the ASH-82T engine for two variants of severe temperature conditions: maximum $t_{cy} = 250^\circ\text{C}$, $t_{\text{ext air}} = 40^\circ\text{C}$ ($t_c = 120^\circ\text{C}$) and minimum $t_{cy} = 150^\circ\text{C}$, $t_{\text{ext air}} = -40^\circ\text{C}$ ($t_c = +40^\circ\text{C}$). Key:

1. Boost pressure, Torr; 2. Excess air coefficient; 3. p_c ; 4. B;
5. Takeoff regime according to specifications; 6. g/l s h; 7. According to specifications; 8. t_c

In order to determine which gasoline is required for an engine, the knocking characteristics are recorded under the most severe temperature conditions (both maximum and minimum t_c and t_{cy}). The characteristics are compared with the values of the required boost for mixture compositions established by specifications for the engine (shaded rectangle in Fig. 27). If the knocking characteristic of a gasoline passes above the required boost ($\bar{p}_c > p_{c\ sp}$), the gasoline is suitable for the given engine in antiknock value, and if it passes below it ($\bar{p}_c < p_{c\ sp}$), it is unsuitable [30, 80, 97].

ANTIKNOCK VALUES

Octane Number

The antiknock value of the aviation gasoline employed should not be below the standards established by testing gasoline on aviation engines. In order to check this, samples taken from each gasoline batch are tested on special one-cylinder units by comparison with standard fuels. The fundamental standard is

isooctane C_8H_{18} , with the carbon skeleton molecular structure $C - \overset{\overset{C}{|}}{C} - C - \overset{\overset{C}{|}}{C} - C -$,

a hydrocarbon with a high antiknock value arbitrarily taken as 100. The second standard used is normal heptane C_7H_{16} , whose low antiknock value is arbitrarily taken as zero. By mixing these two compounds in different proportions, fuel equivalents from zero to 100 are obtained, i.e., a scale of octane number is formed.

The composition of the standard fuel equivalent to the gasoline being tested is found by testing on an IT9-2 unit with an excess air coefficient corresponding

to the maximum knock intensity ($\alpha = 1.0-1.1$). Thus, the octane number of a gasoline is an index of its knocking stability on a lean mixture, equal to the percent (by volume) content of isooctane in a mixture with normal heptane, which in antiknock value under standard testing conditions is equivalent to the given gasoline. The octane number serves to check gasolines with reference to cruise power settings [30, 64, 97].

Rating of Gasolines

At full power settings, when engines operate on a rich mixture ($\alpha \approx 0.6$) for purposes of internal cooling, the antiknock value is usually completely different than on a lean mixture. Moreover, in almost all aviation gasolines (containing an antiknock compound) it is higher than 100, i.e., mixtures of isooctane and heptane as standards are unsuitable on a rich mixture. Standards above 100 are obtained by adding various quantities of the antiknock tetraethyllead to isooctane. The standards are calibrated on a one-cylinder unit (with an aircraft engine cylinder) at $\alpha = 0.6$, and quality grades are established for each of them (Fig. 28, top). Figure 28 shows the power in percent, obtained by increasing the boost before the start of knocking, in relation to isooctane containing no tetraethyllead.

The rating of gasolines is determined on the IT-9-1 unit: it is determined which standard fuel at $\alpha = 0.6$ starts to knock at the same power as the gasoline being tested. The rating of the gasoline is assumed to be equal to that of this standard [30, 64, 97].

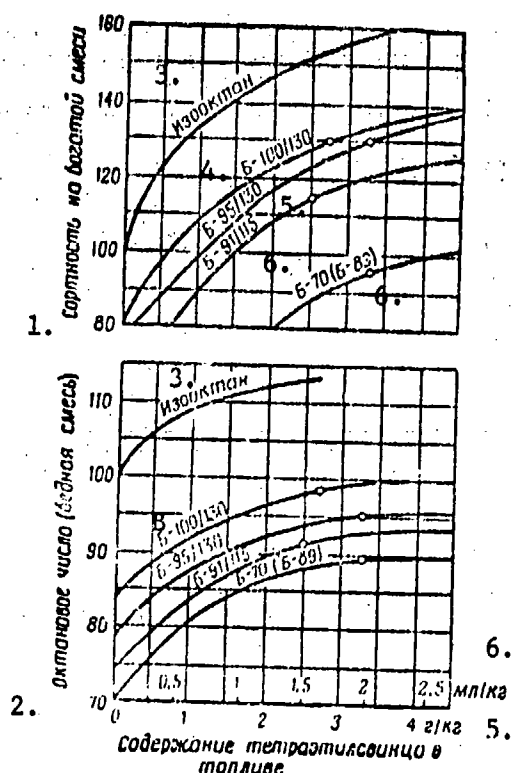


Fig. 28. Effect of TEL on the increase in octane numbers of fuels (bottom) and rating on rich mixture (top). Key:

1. Rating on rich mixture; 2. Octane number (lean mixture); 3. Isooctane; 4. B; 5. g/kg; 6. ml/kg

ANTIKNOCK COMPOUND

Effectiveness

Tetraethyllead $Pb(C_2H_5)_4$, abbreviated TEL, introduced into gasolines as an antiknock compound, is a colorless, very toxic liquid. At $20^\circ C$, its density is 1.652. At $200^\circ C$, it boils and simultaneously decomposes. Addition of small initial amounts of TEL (up to 2.5-3.3 g/kg) is very effective (Fig. 28). A further increase of its content in gasoline does not appreciably raise the antiknock value, but has a negative effect on engine performance (lead oxide deposits increase in the cylinder). In engines with long service lives, it is advisable to use gasolines of lower TEL content or better, to use pure gasolines (provided they have a sufficient antiknock value). TEL is introduced into gasolines in the

composition of the ethyl flued, a mixture with scavengers (brominated and chlorinated hydrocarbons). By reacting with them after burning, lead changes into compounds which are volatile at high temperature, and is thus essentially eliminated from the combustion chamber together with the exhaust gases [48, 81].

Toxicity

Tetraethyllead is a strong poison acting on the nervous system and blood. It is capable of accumulating in the body, and therefore poisoning with this compound may be observed after a long time. Its entry into the digestive tract may result in death. Ethylated gasolines must not be used to wash hands or clothing: after the gasoline evaporates, tetraethyllead remains, and is capable of penetrating into the body through the skin [48, 72].

Stability

TEL is added to gasolines during their production. In prolonged storage of gasoline, tetraethyllead gradually oxidizes, decomposes, and reacts with the hydrocarbon oxidation products. This forms a white sediment (in dry form, a thin, corrosive dust containing 50-60% lead) which may disrupt the normal operation of fuel equipment. It should be kept in mind that this sediment is very toxic. Decomposition of TEL is shown by the turbidity of gasoline. Decomposition of TEL may also lead to knocking in engines. To increase the stability of TEL dissolved in gasoline, a stabilizer, parahydroxydiphenylamine, is added to aviation gasolines in the amount of 40-50 g/t; it inhibits the oxidation decomposition of TEL [60, 66, 83].

GRADES OF AVIATION GASOLINES

Uses and Basic Indices

The standard specifies aviation gasolines of four main grades:

B-100/130 - of a bright orange color, containing TEL in amounts up to 2.7 g/kg, used in ASh-73 TK engines and certain foreign engines;

B-95/130 - yellow, containing TEL up to 3.3 g/kg and designed for ASh-82V and ASh-82T engines;

B-91/115 - green, containing TEL up to 2.5 g/kg and designed for ASh-62IR and AI-26V engines.

In the brand designations of these gasolines, the numerator of the fraction, for example 91, indicates the lower limit of the octane number, and the denominator, for example 115, denotes the lower rich-mixture rating limit allowed for the given gasoline.

B-70 - colorless, with an octane number not below 70, containing no TEL and designed for AI-14R and M-11 engines of various modifications. B-70 gasoline is used as the starting fuel for certain types of gas turbine engines and as the main fuel for special gas turbine units; TEL-containing gasolines cannot be used in such units because of deposition of lead oxides on the turbine blades. The antiknock value of gasoline is of no significance for their operation.

In addition, two more grades of gasolines have limited applications:

BA - with a particularly high antiknock value (lean mixture rating not below 115 and rich-mixture rating not below 160) containing TEL up to 3.3 g/kg; used in

certain foreign engines;

SB-78 - blended gasoline with an octane number not below 78, containing TEL up to 0.66 g/kg and designed for AI-14VF engines. It is prepared by mixing B-70 gasoline (75%) with B-91/115 gasoline (25%).

As a rule, B-70 gasoline is produced by straight-run distillation of crude. Higher grades are prepared by mixing straight-run gasoline fractions and by catalytic cracking with high-octane synthetic components (isoparaaffinic or aromatic ones). For purposes of economy, they are used only in those engine types where they are required. However, if an established grade is lacking, a higher grade may be used provided that it does not contain any more (or significantly more) TEL than the amount adopted for the given engine type [60, 66, 72, 96].

General Properties

In aviation gasolines as well as fuels for gas turbine engines, the content of substances promoting an increased formation of deposits, overheating of engines, and corrosion (gum, unsaturated hydrocarbons, organic acids) is limited; the presence of water-soluble acids and alkalis, water, and mechanical impurities is not permitted. Specific for all aviation gasolines is the strict limitation of the total sulfur content to no more than 0.05%. This is due to the fact that the sulfuric acid formed from the combustion products may enter the oil and accumulate in the crankcase, posing a danger to corrosion-sensitive lead bronze bearings.

Like fuels for jet engines, aviation gasolines must have a low temperature of the start of crystallization (not above -60°C). In order to prevent the formation of ice crystals, the same antiicing additive may be added to aviation gasolines as that added to fuels for jet engines (in the same amounts). However, the danger of crystal formation in gasolines is less than in kerosene-type fuels (despite the higher water solubility limit), since in gasolines ice crystals rapidly settle to the bottom and are removed with the sediment [60, 66].

Foreign Brands

Specifications of the USA, Great Britain, France and other countries provide for aviation gasoline grades 60/87, 91/96, 100/130 and 115/145 (designation based on the octane number and rich-mixture rating (with maximum TEL content up to 2-2.5 g/kg, as well as nonethylated gasoline with octane number 73 [72]).

CHAPTER 5

ROCKET PROPELLANTS

(Based on Foreign Publications)

CONDITIONS OF APPLICATION AND GENERAL ROCKET PROPELLANT REQUIREMENTS

Fundamental Characteristics

Modern rocket engines operate on liquid or solid chemical propellants¹ and are accordingly divided into two groups - liquid rocket engines (LRE) and solid propellant rocket engines (SPRE). The liquid rocket propellant is located in tanks outside the engine; it is supplied by equipping the LRE with a turbopump assembly (Fig. 29) or the gas-pressure (pressurized feeding system. SPRE have no feeding system; a plastic or rubbery mass of solid fuel is placed directly in the combustion chamber.

A rocket propellant burns without consuming oxygen from the surroundings and serves as the only source of the working substance of the rocket engine (the mass of the ejected gas is equal to the mass of the propellant). The content of combustible elements in the rocket propellant is low; most of it consists of oxygen (or fluorine) necessary for their oxidation. Therefore, the liberation of heat per unit weight of the on-board reserve of rocket propellant is several times less than for propellants oxidized with atmospheric oxygen. However, an attempt to use compositions with the highest calorific value h_{α} is not always justified

¹Nuclear propellants of prospective rocket engines (including electric ones) are briefly discussed at the end of Ch. 5.

because of the high temperature of the combustion products (above 2500-3000°C), causing thermal dissociation (breakdown) of their molecules with absorption of thermal energy. The high temperature is explained by the fact that each kilogram of combustion products receives all the heat liberated by a kilogram of rocket propellant (during the combustion of ordinary fuel in air, each kilogram of gas receives not more than 6% of the heat evolved by 1 kg of fuel) [5, 6, 9, 38, 73, 86, 104].

Effect on Specific Thrust

If there were no dissociation, the higher calorific value would cause a correspondingly higher increment of the gas temperature during combustion $\Delta T_z^* = \frac{h_z}{C_p}$ and a higher specific thrust:

$$p_{spid} = \frac{w_{nid}}{g} = 9.33 \sqrt{C_p T_z^* t_z} \quad (5.1)$$

Formula (5.1) expresses the ideal specific thrust which for a theoretical exhaust regime without friction and without heat loss depends only on the ideal exhaust velocity w_{nid} (the actual velocity is approximately 5% lower than the ideal velocity):

$$w_{nid} = \sqrt{\frac{2g}{A} C_p T_z^* \left(1 - \frac{1}{n^{\frac{k-1}{k}}}\right)} = 91.5 \sqrt{C_p T_z^* \eta_{t_z}} \quad (5.2)$$

where C_p is the specific heat of the gas at constant pressure;

T_z^* is the theoretical (ideal) gas temperature after combustion in the absence of dissociation, incompleteness of combustion and heat transfer through the engine walls;

Caption for Fig. 29

Fig. 29. Properties of liquid rocket propellant affecting the performance data of an aircraft, the work process, and the engine performance reliability. Key:

1. Power plant units; 2. TANK WITH OXIDIZER; 3. TANK WITH COMBUSTIBLE;
4. GAS GENERATOR; 5. TURBOPUMP ASSEMBLY; 6. COMBUSTION CHAMBER; 7. NOZZLE;
8. Fuel quality indices (classified according to the power plant units in which their influence is manifested); 9. Parameters, processes and phenomena directly dependent on propellant properties; 10. Dangerous aftereffects and operational performance which may be caused by unsatisfactory propellant quality; 11. Performance indices of aircraft and LRE dependent on fuel; 12. Combat readiness;
13. Flying weight; 14. Payload; 15. Total impulse; 16. Duration of active flight; 17. Maximum speed, range and altitude; 18. Specific thrust; 19. Maximum thrust; 20. Reserve of energy; 21. Weight of propellant; 22. Active oxygen (fluorine) concentration; 23. Oxidizer density; 24. Heat of transformation (or enthalpy) of oxidizer; 25. Propellant losses; 26. Refueling difficulty;
27. Boiling or intense vaporization; 28. Boiling temperature; 29. Freezing temperature; 30. Corrosiveness; 31. Content of inhibitors; 32. Chemical stability; 33. Content of stabilizers; 34. Toxicity; 35. Calorific value (or enthalpy) of combustible; 36. Stoichiometric coefficient; 37. Combustible density; 38. Destruction of filled tanks; 39. Crystallization; 40. Liquid corrosion; 41. Explosion, fire; 42. Decomposition and other transformations;
43. Change in propellant composition; 44. Servicing difficulties; 45. Poisoning, burns; 46. Starting; 47. Gas temperature before TBA turbine; 48. Deposits on TBA turbine; 49. Erosion of TBA blades; 50. Destruction of TBA turbine, engine shutdown; 51. Spontaneous combustibility; 52. Rich flameout limit;
53. Carbon content; 54. Condensed combustion products; 55. Behavior fluctuations; 56. Breakdown of pumps; 57. Cavitation; 58. Vapor lock;
59. Boiling temperature; 60. Viscosity (at low temperature); 61. Underpressure at inlet; 62. Crystal formation at low temperature; 63. Freezing temperature;
64. Emulsified water; 65. Decrease of propellant injection, change in mixture composition, reduction of thrust; 66. Clogging of injectors by solid particles;
67. Sticky deposits; 68. Mechanical impurities; 69. Gum; 70. Viscosity;
71. Density; 72. Surface tension; 73. Fineness of spray and mixing; 74. COMBUSTION CHAMBER HEAD; 75. Enthalpy of combustion products; 79. Calorific value (or enthalpy) of fuel; 80. Molecular weight of combustion products (heat capacity, gas formation); 81. Elemental composition; 82. Number of atoms in molecules of combustion products; 83. Self-ignition delay; 84. Starting; 85. Explosion on starting; 86. Regime fluctuation. Locking, explosion; 87. Combustion instability; 88. Flame radiation; 89. Time of chemical transformation; 90. Carbon content; 91. Condensed combustion products; 92. COOLING JACKET; 93. Heat capacity; 94. Thermal conductivity; 95. Viscosity; 96. Density; 97. Boiling temperature; 98. Content of additives; 99. Thermal stability; A. Coefficient of heat transfer from walls to cooling component; B. Temperature rise and burn-out of walls; C. Decrease of fuel injection, change in mixture composition, reduction of thrust; D. Destruction of nozzle; E. Cooling regime (vapor formation at walls); F. Deposits; G. Erosion of walls; H. Gaseous corrosion; I. Condensed combustion products; J. Corrosiveness of combustion products; K. Enthalpy of escaping gases; L. Recombination of the molecules of combustion products; M. Thermal expansion efficiency; N. Elemental composition; O. Number of atoms in the molecules of combustion products.

π_n is the gas pressure drop at the rocket engine nozzle;

k is the specific heat ratio of the process of gas expansion in the nozzle;

$g = 9.81 \text{ m/sec}^2$ is the acceleration due to gravity;

$A = 1/427 \text{ kcal/kg}$ is the thermal equivalent of mechanical energy;

$\eta_{\text{th}} = 1 - \frac{1}{\frac{k-1}{k}}$ is the thermal efficiency.

Actually, however, a rise in temperature T^*_z leads to an increased dissociation. As a result, before entering the nozzle, the gas has a reserve of chemical energy that has not been converted to thermal energy. This reserve is greater the higher the temperature T^*_z . As the gas expands in the nozzle, it cools, the dissociated molecular fragments combine, and the chemical energy completes its conversion into thermal energy, so that the gas temperature T_n at the exit from the nozzle is higher than in the absence of dissociation. Correspondingly lower is the thermal efficiency

$$\eta_{\text{th}} = \frac{C_p T^*_z - C_p T_n}{C_p T^*_z},$$

expressing the fraction of enthalpy $C_p T^*_z$ converted into kinetic energy (since $C_p T_n$, the enthalpy of the gas expelled to the outside, is higher); in the final analysis, the specific thrust obtained according to Eq. (5.1) is lower. This decrease in efficiency is sometimes conventionally expressed as a decrease in the specific heat ratio (to $k = 1.1-1.2$) in formula (5.2). Hence, suitable rocket propellants are those whose combustion products have moderate temperatures and hence have less tendency to dissociate, and also contain mainly diatomic molecules, which are stable to dissociation [55, 73, 100].

Role of the Properties of Combustion Products

For the same calorific value h_x , the gas temperature T^*_z is lower the higher the specific heat $C_p \frac{C_{pm}}{\mu}$, i.e., the smaller the molecular weight of the combustion products (in molar heat capacity C_{pm} , the difference between gases is much smaller than in molecular weights). An increase in C_p or the gas constant $R = \frac{848}{\mu}$ [kgm/kg deg] and in gas formation of the propellant $v_{pr} = \frac{22.4}{\mu}$ [nm³/kg] not only compensates the effect of temperature lowering on the specific thrust, but also provides for an increase in specific thrust owing to the increase in efficiency.

In order to obtain low-molecular combustion products (with a small μ), a propellant with an oxidizer deficiency is usually employed, $\lambda = 0.7-0.8$, and in the case of an oxygen-hydrogen propellant, even $\lambda = 0.4$ (Fig. 30), i.e., incomplete combustion of the propellant and the associated decrease of its calorific value h_x are deliberately aimed at. A certain amount of free hydrogen H_2 ($\mu = 2$) instead of water vapor H_2O ($\mu = 18$), and also carbon monoxide CO ($\mu = 28$) instead of carbon dioxide CO_2 ($\mu = 44$) yields a gain in the degree of energy utilization (in efficiency η_{t_z}) which covers this decrease. The molecular weight of the combustion products of hydrogen is lower than that of the combustion products of carbon and other combustible elements.

Thus, a high calorific value per se, let alone a high combustion temperature, fails to indicate a high energy efficiency of the propellant in a rocket engine, since these quantities do not reflect the degree of utilization of the propellant energy, which is dependent on the properties of the propellant itself [5, 86]. An index expressing its influence is the specific thrust (unit of impulse propellant). It should be kept in mind that this index is relative, since it depends

on factors other than the propellant. For modern chemical fuels, the velocity of the gas exhaust from the nozzle of rocket engines is on the order to 2-4 km/sec, and the specific thrust is correspondingly of the order of 200-400 kg sec/kg [55, 73, 86].

Role of Propellant Density

In addition to the specific thrust, a decisive influence on the velocity, altitude and range of flight of a rocket vehicle is exerted by the mass of the rocket propellant consumed, or more accurately, its fraction with respect to the mass of the vehicle in accordance with the formula for the thrust force impulse (1.12); it depends on the propellant density. If the entire impulse is used up only in accelerating the rocket vehicle, the maximum velocity is expressed by Tsiolkovskiy's formula

$$v_{\max} = g_{\text{Psp}} \ell_n \frac{G_i}{G_{fi}}. \quad (5.3)$$

For a given payload G_p , weight G_0 of the empty rocket vehicle, propellant volume V_{pr} and initial weight $G_i = G_0 + G_p + V_{\text{pr}} \rho_{\text{pr}}$ changing in accordance with the propellant density ρ_{pr} ,

$$v_{\max} = g_{\text{Psp}} \ell_n \left(1 + \frac{V_{\text{pr}}}{G_0 + G_p} \rho_{\text{pr}} \right). \quad (5.4)$$

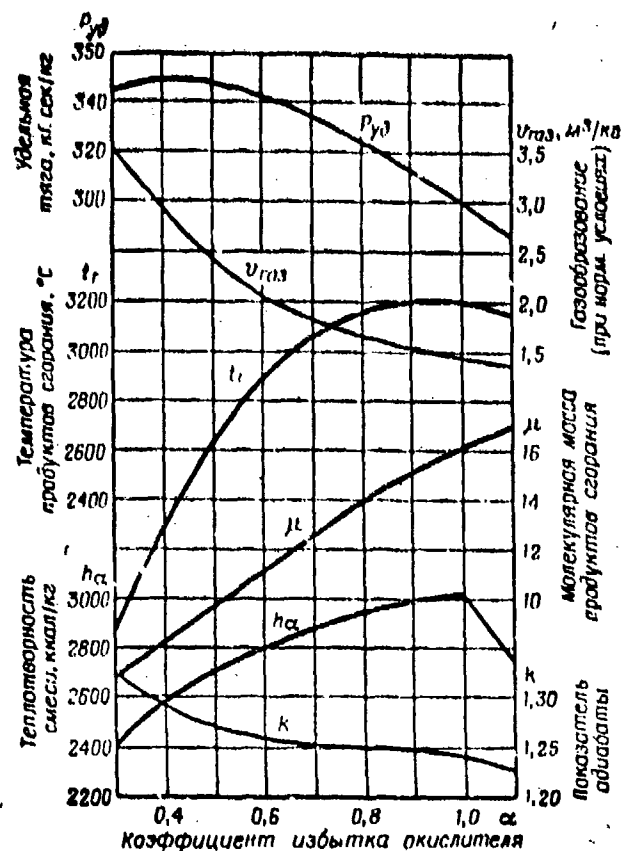


Fig. 30. Calculated characteristics of the propellant, liquid oxygen + liquid hydrogen according to the mixture composition at $p_k = 21 \text{ kg/cm}^2$ $T_{exp} = 20.3$). Key:

1. Calorific value of mixture, kcal/kg;
2. Temperature of combustion products, °C;
3. Specific thrust, kg sec/kg; 4. P_{sp} ;
5. v_{gas} ; 6. Specific heat ratio;
7. Molecular weight of combustion products;
8. Gas formation (at standard conditions);
9. v_{gas} , m^3/kg ; 10. Excess oxidizer coefficient.

The effect of increase in propellant density is greater for small $\frac{V_{pr}}{G_0 + G_p}$, i.e., for a flying vehicle of small and medium range, a heavier propellant may turn out to be more appropriate, even if it generates a smaller specific thrust (for example, solid propellant or nitric acid propellant in comparison with oxygen propellant). Flying vehicles with a large relative propellant capacity obtain a smaller percent gain in velocity owing to an increase in the impulse expended in accelerating the mass of a heavier propellant.

If the initial weight has been established, and the payload changes in accordance with the propellant density $G_p = G_1 - G_0 - V_{pr}\rho_{pr}$, then

$$V_{\max} = gP_{sp} \ell_n \frac{1}{1 - \frac{V_{pr}}{G_1} \rho_{pr}}. \quad (5.5)$$

Moreover, the density increase effect (Fig. 6) is greater for flying vehicles with a long flight range (with a large propellant capacity referred to a unit of the initial flying weight). However, this effect is obtained at the expense of a decrease in payload.

An on-board reserve of propellant of the same weight requires a capacity that is inversely proportional to the propellant density: $V'_{pr} = V_{pr} \frac{\rho_{pr}}{\rho}$. The difference in the required capacities of rocket vehicles is practically always important, since rocket propellants of different compositions may differ markedly (severalfold) in density [55, 73, 86, 100].

ROCKET PROPELLANT REQUIREMENTS

The variety of chemical compositions of rocket propellants is due to the fact that some of them have advantages in certain applications and others are preferable for other problems. This does not permit a specific formulation of unique requirements for all types of rocket propellants (liquid and solid, mono- and bipropellants, high-boiling and cryogenic propellants, etc.). All rocket propellants are usually subjected to only a few relatively general requirements, chief of which are:

- 1) high specific thrust, reached as a result of an optimum combination of a high calorific value of the propellant, low molecular weight, and small number of atoms in the molecules of the combustion products;
- 2) high density;
- 3) not too high combustion temperature;
- 4) a normal course of the work process (safe ignition on starting, fast and complete chemical transformation, stability of combustion process);
- 5) combat readiness (possibility of keeping the vehicle in the fueled state, possibility of use in a wide range of climatic and weather conditions).

The chemical reactivity of rocket propellants is the cause of undesirable properties, i.e., explosion hazard, instability (decomposition), corrosiveness to materials, and toxic effects on humans. As a rule, rocket engines are designed for a few seconds or a few minutes of operation, and it is entirely satisfactory if people can tolerate the untoward effects of a rocket propellant during that period of time [9, 29, 38, 55, 78, 86].

LIQUID BIPROPELLANTS

Propellant Groups

A bipropellant is usually employed in LRE. Its components, the fuel and the oxidizer, are located in separate tanks and are mixed only after being supplied to the combustion chamber. As a rule, the consumption of the oxidizer is several times as high as that of the fuel. The properties of a rocket propellant are determined to a larger extent by the oxidizer than by the fuel. For this reason, LRE propellants are divided into groups according to the oxidizer components

entering into their composition: nitrogen components (the oxidizers are nitric acid and nitrogen oxides), oxygen components (based on liquid oxygen), and hydrogen peroxide and fluorine components (based on liquid fluorine and fluorine compounds) [15, 73, 100].

Ratio of the Components

The stoichiometric ratio of the oxidizing to the combustible component (corresponding to $\alpha = 1$) depends on the elemental composition of the oxidizer and fuel. The required quantity of oxygen-containing oxidizers constituting "dilute" oxygen is greater than the quantity of pure oxygen by a factor of $1/[O]_{act}$, where $[O]_{act}$ is the weight of active oxygen which gives up 1 kg of oxidizer to the fuel. If the oxidizer contains no combustible elements, the entire oxygen present in the oxidizer $[O]_{ox} = [O]_{act}$ is active. If however 1 kg of oxidizer contains $[C]_{ox}$ kg of carbon and $[H]_{ox}$ kg of hydrogen, part of the oxygen will remain bound to them, and the quantity of active oxygen will be smaller:

$$[O]_{act} = [O]_{ox} - 2.66[C]_{ox} - 7.94[H]_{ox} \quad (5.6)$$

The required quantity of oxidizer containing water is even greater: the weight of active oxygen in this case is multiplied by the oxidizer concentration $K < 1$.

If fluorine F_2 is used as the oxidizer, the calculations should be carried out by considering that the atomic weight of fluorine (19.00) is 1.19 times greater than that of oxygen and that fluorine is univalent, i.e., the oxidation of fuel requires twice as many fluorine atoms F than divalent oxygen atoms O. Hence, $1.19 \times 2 = 2.38$ times more fluorine is required.

Ratios of the required quantity of certain oxidizers to the required quantity of oxygen, calculated from formula (5.6), are listed in Table 8.

1. Окислитель	2. Молекулярная масса	3. Элементарный состав, кг/кг		6. Отдача окислительных элементов в кг на 1 кг окислителя		9. Потребное количество по отношению к кислороду
		4. кислорода [O] _{ок}	5. водорода [H] _{ок}	7. кислорода [O] _{акт}	8. фтора [F] _{акт}	
10. Кислород (O ₂)	32,00	1	—	1	—	1
Воздух (23,1% O ₂)	29,01	0,231	—	0,231	—	4,33
Азотная кислота (100% HNO ₃)	62,02	0,762	0,016	0,635	—	1,58
Азотная кислота (98% HNO ₃)	—	—	—	0,623	—	1,61
Азотный тетроксид (N ₂ O ₄)	92,02	0,696	—	0,696	—	1,44
Перекись водорода (100% H ₂ O ₂)	34,02	0,941	0,059	0,470	—	2,13
Перекись водорода (90% H ₂ O ₂)	—	—	—	0,423	—	2,36
Перекись водорода (80% H ₂ O ₂)	—	—	—	0,376	—	2,66
Фтор (F ₂)	38,00	—	—	—	1	2,38
Дифторид кислорода (OF ₂)	54,00	0,457	—	0,457	0,543	1,46

Table 8. Oxidizing efficiency and required quantity of liquid oxidizers in comparison with oxygen. Key:

1. Oxidizer; 2. Molecular weight; 3. Elemental composition, kg/kg; 4. of oxygen [O]_{ox}; 5. of hydrogen [H]_{ox}; 6. Yield of oxidizing elements in kg per 1 kg of oxidizer; 7. Oxygen [O]_{act}; 8. Fluorine [F]_{act}; 9. Required quantity in relation to oxygen; 10. Oxygen (O₂)

Air (23.1% O₂)

Nitric acid (100% HNO₃)

Nitric acid (98% HNO₃)

Nitrogen tetroxide (N₂O₄)

Hydrogen peroxide (100% H₂O₂)

Hydrogen peroxide (90% H₂O₂)

Hydrogen peroxide (80% H₂O₂)

Fluorine (F₂)

Oxygen difluoride (OF₂)

In the case of a fuel containing no boron or metals, and an oxygen-containing oxidizer, the stoichiometric ratio is determined by a formula resulting from (1.2) and (5.6):

$$x_0 = \frac{2.66[C]_f + 7.94[H]_f - [O]_f}{[O]_{ox} - 2.66 [C]_{ox} - 7.94 [H]_{ox}},$$

where the symbols of elements in the square brackets denote their content in the fuel component (numerator) and oxidizing component (denominator).

Example. A bipropellant consisting of the oxidizer nitric acid HNO_3 containing $[O]_{ox} = 0.762$ and $[H]_{ox} = 0.016$, and the fuel dimethylhydrazine $(\text{CH}_3)_2\text{N}_2\text{H}_2$, which contains $[C]_f = 0.400$ and $[H]_f = 0.133$, burns completely when the ratio of the components is

$$x_0 = \frac{2.66 \cdot 0.400 + 7.94 \cdot 0.133}{0.762 - 7.94 \cdot 0.016} = 3.34.$$

In practice, the oxidizer composition has a decisive influence on this quantity.

As a rule, the actual ratio of the components $x = ax_0$, is lower than the stoichiometric ration [5, 86]: in the combustion chambers, in order to obtain the maximum thrust, the propellant burns at $\alpha \approx 0.4 - 0.8$; and in gas generators of propellant supply systems operating on the main components of the propellant (Fig. 29), in order to lower the gas temperature, at $\alpha \approx 0.1 - 0.2$ [8, 55, 73].

Energy Content

The maximum amount of heat that can be theoretically liberated by 1 kg of rocket propellant in the presence of exothermic reactions proceeding to completion and cooling of the combustion products to the initial temperature is called the energy content of the propellant. The energy content of a bipropellant of stoichiometric composition is taken per unit of total weight of the components. It depends on the energy content of the fuel H_f (in the reaction with the oxygen of the rocket oxidizer, the fuel evolves as much heat as it generates during combustion in air, see Table 2), on the stoichiometric ratio of the components, and on the thermal effect of transformation of the oxidizer H_{ox} :

$$h_{rp} = \frac{H_f + \chi_0 H_{ox}}{1 + \chi_0} \text{ [kcal/kg]} \quad (5.7)$$

1. Окислитель	2. Теплота образования при 20°С, ккал/кг	3. Полная энтальпия i_{ox} , ккал/кг	4. Тепловой эффект H_{ox} , ккал/кг	5. Плотность ρ , кг/л	Температура, °С	
					6. кипения	7. замерзания
8. Жидкий кислород (O_2)	0	-96	-96	1,14	-183	-218
Жидкий озон (O_3)	+730	+630	+630	1,35	-112	-193
Азотная кислота (HNO_3)	-660	-660	-200	1,51	+84	-41
Азотный тетроксид (N_2O_4)	-50	-50	-50	1,45	+21	-11
Перекись водорода (H_2O_2)	-1315	-1315	+380	1,45	+150	-1
Жидкий фтор (F_2)	0	-80	-80	1,51	-188	-219
Дифторид кислорода (OF_2)	+140	+70	+70	1,52	-145	-223

Table 9. Thermal effect and certain physical properties of anhydrous oxidizing components of rocket propellants. Key: (1, H_{ox} , ρ at 20°C; for cryogenic components, at the boiling point) [9, 15]. Key:

1. Oxidizer; 2. Heat of formation at 20°C, kcal/kg; 3. Total enthalpy i_{ox} , kcal/kg; 4. Thermal effect H_{ox} , kcal/kg; 5. Density ρ , kg/ ; 6. B.P., °C; 7. F.P. °C; 8. Liquid oxygen (O_2)
 Liquid ozone (O_3)
 Nitric acid (HNO_3)
 Nitrogen tetroxide (N_2O_4)
 Hydrogen peroxide (H_2O_2)
 Liquid fluorine (F_2)
 Oxygen difluoride (OF_2)

Oxidizers in the form of gaseous elements (oxygen O_2 , fluorine F_2) have zero enthalpy but in liquid form oxygen ($t = -183^\circ C$) and fluorine ($t = -188^\circ C$) have negative enthalpy, and give a negative thermal effect H_{ox} , since their vaporization and heating consume a part of the heat evolved by the combustion. For composite oxidizers as well as combustible components, the thermal effect depends not only on enthalpy (heat of decomposition), but also on their content of combustible elements, and may be calculated from formula (1.5). A majority of complex oxidizers also give a negative thermal effect H_{ox} .

The effect of the thermal effect of water present in the oxidizer (-600 kcal/kg) is considered, as in the case of combustibles.

Example. Determine the energy content of the rocket propellants dymethylhydrazine + liquid oxygen and dimethylhydrazine + nitric acid. The energy content of dimethylhydrazine $H_f = 7140$ kcal/kg, the thermal effect of 1 kg of oxidizers for liquid oxygen $H_{ox} = -96$ kcal/kg, and for nitric acid $H_{ox} = -200$ kcal/kg (from Tables 1 and 9). The stoichiometric coefficient of dimethylhydrazine with oxygen $\chi_0 = 2.12$ (from Table 7), with nitric acid $\chi_0 = 3.34$ (see the example above). The energy content is determined from formula (5.7) for a stoichiometric mixture of dimethylhydrazine with oxygen

$$h_{rp} = \frac{7140 + 2.12 (-96)}{1 + 2.12} = 2220 \text{ kcal/kg}$$

and with nitric acid

$$h_{rp} = \frac{7140 + 3.34 (-200)}{1 + 3.34} = 1430 \text{ kcal/kg}$$

The energy content of certain rocket propellants is given in Table 10. It substantially depends on the oxidizer employed, and is less dependent on the

fuel. For example, for the propellant kerosene + liquid oxygen, $h_{rp} = 2260$ kcal/kg, which is only 2% higher than for the propellant dimethylhydrazine + liquid oxygen, whereas the energy content of kerosene is 45% higher than for dimethylhydrazine. Moreover, dimethylhydrazine provides a higher specific thrust owing to the lower molecular weight of the combustion products. The effective calorific value h_{α} of a rocket propellant for $\alpha < 1$ is less than the calculated energy content (see Fig. 4) [16, 73, 86, 97].

Calculated Density

The density (or specific gravity) of a bipropellant is a conventional, theoretical parameter, since the oxidizer and fuel are stored and fed into the combustion chamber separately. For an effective ratio of the components κ , this ratio of the sum of the weights of the fuel and oxidizer $1 + \kappa$ to the sum of their volumes $V_f + V_{ox} = \frac{1}{\rho_f} + \frac{\kappa}{\rho_{ox}}$:

$$r_p = \frac{1 + \kappa}{\frac{1}{\rho_f} + \frac{\kappa}{\rho_{ox}}} \quad (5.8)$$

For a uniform mixing of the fuel and oxidizer to take place, it is desirable that their volume flow rates be similar, i.e., the ratio $\frac{\kappa}{\rho_{ox}} : \frac{1}{\rho_f} \frac{\kappa f}{\rho_{ox}}$ be as close as possible to unity; the oxidizer density should be higher than the fuel density wherever possible [26, 86, 97].

Ignition

On contact between the self-igniting components injected into the combustion chamber, a hot vapor-gas is formed, i.e., a mixture of chemically active products

of their decomposition and vapors. The development of reactions in the vapor-gas gives rise to flame kernels which rapidly spread through the entire mass of the accumulated fuel mixture. At the same time, the pressure increases sharply, and an explosion ("full start") takes place. The longer the self-ignition delay, the higher the pressure peak. It is estimated that in order to avoid engine failure, the self-ignition delay should be no longer than 0.03 sec. In normal operation of LRE, a decrease of the delay in chemical transformation of the propellant increases the combustion stability and promotes a decrease in pressure fluctuations. When nonhypergolic basic components (Oxygen propellants, nitric acid + kerosene) are used, self-igniting starting components are sometimes used for the formation of the initial flame kernel [10, 29, 73, 100].

1. Состав топлива			2. При $\alpha = 1$			3. При оптимальном соотношении компонентов						
4. Окислитель	5. Горючее	6.	7. Стехиометрическое соотношение, α	7. Расчетная плотность $\rho_{p, \gamma}$, г/см ³	8. Теплотворная способность H_o , ккал/кг	9. Коэффициент избытка окислителя α	7. Расчетная плотность $\rho_{p, \gamma}$, г/см ³	10. Молекулярная масса $M_{\text{пр}}$, г/моль	11. Температура продуктов сгорания $T_{\text{пр}}$, °K	12. Показатель расширения λ	Удельная тяга $P_{\text{уд}}$ (кг·сек/кг) при $p_{\text{к}} = 68$ атмосфер	
											13. $P_c - P_H = 1$ атмосфера	14. $P_c - P_H = 40$, $P_H = 0$
16. Азотная кислота	21. Керосин ¹		5,36	1,34	1450	0,92	1,33	25,7	3147	1,22	263	312
	22. Тонка		4,67	1,33	1480	0,91	1,32	26,5	3120	1,23	267	315
	23. Гидразин		1,57	1,27	1420	0,96	1,25	20,9	3021	1,25	279	327
	24. Диметилгидразин		3,31	1,25	1430	0,90	1,22	23,6	3147	1,23	272	321
17. Азотный тетроксид	21. Керосин ¹		4,88	1,29	1790	0,83	1,29	25,5	3438	1,25	276	326
	23. Гидразин		1,44	1,23	1650	0,93	1,22	20,8	3247	1,26	291	342
	24. Диметилгидразин		3,05	1,21	1720	0,84	1,17	23,5	3415	1,25	285	337
	25. Азрозин ²		2,24	1,23	1680	0,88	1,20	22,5	3300	1,25	287	339
18. Жидкий кислород	21. Керосин ¹		3,40	1,05	2260	0,74	1,07	23,7	3686	1,25	300	358
	26. Жидкий аммиак ¹		1,41	0,89	1630	0,96	0,88	19,0	3073	1,23	294	352
	24. Диметилгидразин ¹		2,12	1,00	2220	0,80	0,98	21,5	3608	1,25	310	368
	27. Жидкий n-водород ¹		7,94	0,43	2990	0,50	0,28	10,0	2977	1,26	391	456
19. Перекись водорода	21. Керосин		7,23	1,33	1585	0,96	1,34	22,0	3006	1,20	278	330
	23. Гидразин		2,13	1,27	1530	0,98	1,26	19,4	2927	1,22	287	338
	24. Диметилгидразин		4,51	1,26	1610	0,97	1,24	21,1	3008	1,21	284	336
	28. Пентаборан		6,45	1,23	2480	0,51	1,02	18,1	2969	1,21	309	373
20. Жидкий фтор	26. Жидкий аммиак		3,36	1,18	2300	0,94	1,17	19,0	4517	1,33	359	423
	23. Гидразин		2,33	1,32	2430	0,99	1,32	19,5	4727	1,33	364	429
	28. Пентаборан		7,20	1,29	3670	0,63	1,20	21,8	5080	1,30	361	431
	27. Жидкий n-водород		18,9	0,75	3090	0,43	0,47	12,1	3988	1,33	412	478

29. ¹ Требуется принудительное воспламенение.

30. ² Смесь 50% гидразина и 50% диметилгидразина.

Table 10. Theoretical characteristics of certain liquid bipropellants [60, 86].

Caption for Table 10.

Table 10. Theoretical characteristics of certain liquid bipropellants [60, 86]. Key:

1. Propellant composition; 2. At $\lambda = 1$; 3. At optimum ratio of components; 4. Oxidizer; 5. Fuel, 6. Stoichiometric ratio, λ_0 , 7. Calculated density ρ_{rp} , kg/ ; 8. Energy content h_{rp} , kcal/kg; 9. Excess oxidizer coefficient α ; 10. Molecular weight of combustion products M_{cp} ; 11. Temperature of combustion products T_{cp} , °K; 12. Expansion ratio k ; 13. Specific thrust P_{sp} [kg sec/kg] at $p_c = 68$ atmospheres; 14. $p_n = p_H = 1$ atmosphere; 15. $F_n/F_{cr} = 40$, $p_H = 0$; 16. Nitric acid; 17. Nitrogen tetroxide; 18. Liquid oxygen; 19. Hydrogen peroxide; 20. Liquid fluorine; 21. Kerosene¹; 22. Tonka; 23. Hydrazine; 24. Dimethylhydrazine; 25. Aerozine²; 26. Liquid ammonia¹; 27. Liquid p-hydrogen¹; 28. Pentaborane; 29. ¹Forced ignition is required; 30. ²Mixture of 50% hydrazine and 50% dimethylhydrazine.

Cooling Properties

The combustion chambers and LRE nozzles are cooled by one of the components or separately by both components of the propellant (LRE which operate for a few seconds or in pulses are not cooled). Heat is removed from the hot wall as a result of boiling of a thin layer of coolant directly adjacent to the wall. The vapor bubbles formed condense in the stream of liquid and give up their heat to it. It is therefore desirable that the cooling component have a high heat of vaporization, heat capacity, thermal conductivity, and a sufficient but not excessive boiling point (if it is above 250°C - 300°C, overheating of the chamber dangerous to its strength takes place). It must not decompose on heating or form deposits inside the cooling jacket.

The amount of heat which can be absorbed by 1 kg of the fuel component (heat susceptibility of the component) is determined from the formula

$$q = C(t_b - t_{en}) \quad (5.9)$$

where C is the heat capacity of the liquid:

t_b is its boiling or decomposition temperature;

T_{en} is the temperature at the entrance of the cooling jacket [10, 55, 90, 100].

OXIDIZING COMPONENTS OF LIQUID ROCKET PROPELLANTS

Nitrogen Oxidizers

Nitric acid HNO_3 is a relatively heavy liquid of low viscosity. In content of active oxygen (63.5%) and physical properties (Table 8), it is a useful oxidizer and coolant. Its boiling point at the pressure created in the cooling system by the pressurizing units exceeds 200°C , the heat capacity is around 0.5 kcal/kg deg (above that of most fuels), and the supply is 3-4 times greater than that of the fuel. Its chief disadvantages are its corrosiveness toward most materials and its toxicity. Certain corrosion inhibitors introduced into nitric acid form deposits inside the cooling jacket, and in the absence of inhibitors, deposits are formed from the corrosion products. Concentrated nitric acid is hygroscopic and "fumes" in air (its vapor forms fog droplets with atmospheric moisture). It is chemically unstable and evolves oxygen and nitrogen dioxide NO_2 , which gives the acid its yellow color. The possibility of extensive application of nitric acid in rocketry is due to the large scale and low cost of its production. The introduction of 15-30% nitrogen tetroxide and corrosion inhibitors into nitric acid further improves its desirable qualities (including physical properties, see Fig. 31) and attenuates its corrosiveness and tendency to decompose.

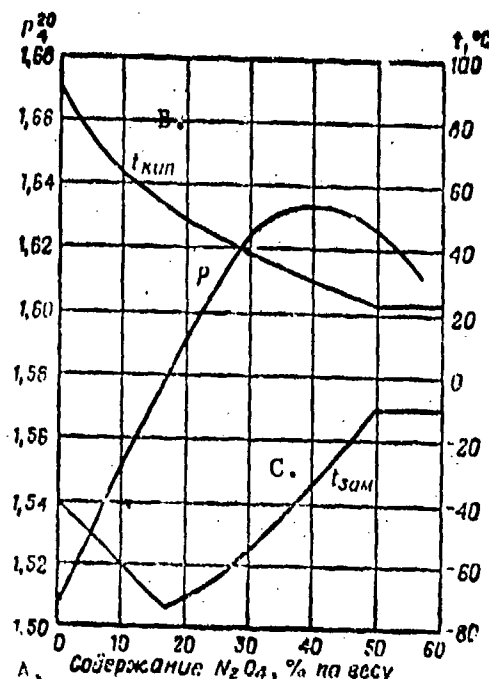


Fig. 31. Density and freezing and boiling temperatures of mixtures of nitric acid HNO_3 with nitrogen tetroxide N_2O_4 (mixture containing over 50% N_2O_4 separate into layers). Key:

A. N_2O_4 content, % by weight
B. t_b ; C. t_{fr}

Nitrogen tetroxide N_2O_4 contains more active oxygen (69.6%) than nitric acid, and its decomposition in contact with a fuel requires less heat; both factors increase the energy content of the propellant. The physical properties of the pure form of nitrogen tetroxide are inferior to those of nitric acid: lower boiling point, higher freezing point, and lower density (Table 8). An important quality of dry nitrogen tetroxide is the fact that it does not corrode metals. Tanks containing tetroxide should be sealed to avoid the penetration of moisture and the spreading of its very toxic vapors [10, 15, 23, 56, 73, 86].

Liquid Oxygen

Liquid oxygen was first proposed as an oxidizing component of rocket propellants by K. E. Tsiolkovskiy when he was developing the initial designs of space rockets back in 1903. The high parameters of oxygen propellants and the simplicity and low cost of liquid oxygen production determined its use for engines of modern rockets carrying space objects. Liquid oxygen O_2 has a light blue color, and its boiling point at atmospheric pressure is $-183^\circ C$. Under pressure, it can have a higher boiling point (up to $-119^\circ C$ at 49.7 kg/cm^2 , the critical point). Crystallization of oxygen takes place at $-219^\circ C$, which makes it possible to supercool oxygen in order to decrease its loss during storage and refueling and prelaunch checking of rockets, and also to increase the weight of the charge (supercooled oxygen has a higher density). Liquid oxygen is not corrosive, but at the low temperature characterizing it (as well as other cryogenic components), many materials become brittle. An important disadvantage of liquid oxygen is its inefficiency in cooling the engine chamber [10, 15, 56, 104].

FUEL COMPONENTS OF LIQUID ROCKET PROPELLANTS

Hydrocarbon Fuels

For auxiliary aircraft LRE, it is convenient to use standard aviation grades of hydrocarbon fuels with hydrogen peroxide oxidizer, which provides for their self-ignition (American LRE Rocketdyne AR2-3, British LRE "Bristol-Siddeley" BS-605, etc.). On the American oxygen LRE "Rocketdyne" F-1 with a thrust of 680 tons (five such engines are clustered in the first stage of the Saturn V rocket), the fuel component is RP-1 kerosene, which boils in the range $185-275^\circ C$ and has a low content of aromatic hydrocarbons (not more than 5%). It is marked by a high combustion

efficiency and a relatively low degree of blackness (radiation) of the flame. The density of this kerosene is 0.795-0.810. Hydrocarbon fuels do not self-ignite with liquid oxygen and require a special device for their ignition [6, 56, 73, 90].

Nitrogen-Containing Fuels

The advantage of nitrogen-containing fuels over hydrocarbon ones is their spontaneous combustibility with nitrogen oxidizers; they are characterized by a higher gas formation (see Table 4), tanks to which a higher specific thrust of LRE can be obtained at a lower temperature. Practical applications have been found abroad for ammonia, its hydrocarbon derivatives - amines (mainly xylidine and triethylamine), and hydrazine and its hydrocarbon derivatives - dimethylhydrazine and methylhydrazine (see Table 3).

Ammonia, the simplest nitrogen hydride NH_3 , is a gas under normal conditions, but at a pressure of 6-7 atmospheres remains liquid at room temperature. In the American LRE Thiokol LR99-RM-1 of the X-15 experimental airplane, liquid ammonia is used in combination with liquid oxygen; electric ignition is used for initiating its combustion.

The name Tonka is applied to a mixture of 50% xylidine and 50% triethylamine (its percentage composition is close to the optimum composition providing for the minimum self-ignition delay), used as the fuel component, which readily self-ignites with nitric acid. Xylidine (aminoxylene) $\text{C}_6\text{H}_3\text{NH}_2(\text{CH}_3)_2$ is a relatively heavy, high-boiling oily liquid, and triethylamine $\text{N}(\text{C}_2\text{H}_5)_3$ is a lighter, volatile liquid. Like most amines, they have an unpleasant odor and are lethal poisons. In comparison with other amines, triethylamine has a stronger injurious

effect on the central nervous system. The density of Tonka is about 0.85. Tonka was first used in German LRE during World War II.

Hydrazine N_2H_4 is a viscous, relatively heavy, poisonous liquid. Its freezing point $+2^\circ C$ is operationally unsatisfactory and for this reason hydrazine is usually employed in a mixture with low-freezing hydrocarbon derivatives. A characteristic feature of hydrazine is the small amount of oxygen it requires - a kilogram per kilogram. In pure form, hydrazine is used as a monopropellant. Unsymmetric¹ dimethylhydrazine $(CH_3)_2N_2H_2$ (abbreviated UDMH) is one of the most important fuel components in modern rocketry. In particular, it is used in the American nitric acid engines Bell LR81-BA-13 of the Atlas Agena rocket, etc. UDMH is an opaque, colorless liquid of low viscosity with a density close to that of kerosene, highly volatile, with a pungent odor and a strong toxic action. UDMH dissolves readily in ethyl alcohol, gasoline, kerosene, and water; it is hygroscopic. Its vapor is explosive over a wide concentration range. A mixture of 50% hydrazine and 50% UDMH, called aeroxine, is used as the propellant in many American LRE (Aerojet engines for all three stages of the Tital 3C rocket, landing and take-off stages of the lunar module of the Apollo system, etc.). The oxidizer in these LRE is nitrogen tetroxide. In energetic and physical properties, aeroxine is intermediate between its two components. Methylhydrazine $CH_3N_2H_3$ is superior to other hydrazine propellants in a number of physical properties (see Table 3).

¹The unsymmetric character of its molecules consists in the fact that two methyl groups are joined to one of the nitrogen atoms, and two hydrogen atoms are joined to the other nitrogen.

It is used in LRE of the maneuvering system of the American Surveyor spacecraft (oxidizer, nitrogen oxides) and in the United Technology experimental fluorine LRE (in a mixture with hydrazine and water [6, 10, 15, 60, 73, 86]).

Liquid Hydrogen

As a component of rocket propellants, hydrogen was proposed by K. E. Tsiolkovskiy in his initial papers in 1903. Hydrogen differs markedly from all other liquid fuel components in physicochemical properties (see Table 3): its boiling point at atmospheric pressure is only 20° above absolute zero, and its density is 10-15 times, and viscosity, thousands of times lower than those of ordinary fuels at their service temperature (0.00018 centipoises, or 0.0025 cS.). Hydrogen provides the high-energy characteristics of a rocket propellant (see Table 10) and a convenient arrangement of the work process: its combustion rate with oxygen and fluorine is very high, the combustion process is stable, the thermal radiation of the flame is negligibly low, and no scale or deposits are formed in the combustion chamber and cooling system. Incomplete combustion of hydrogen does not adversely affect the parameters of the process, but improves them (see Fig. 30). For this reason, the work process is deliberately designed for a large excess of oxygen (up to $\alpha = 0.4$, i.e., the amount of nonburning hydrogen supplied is 1.5 times the amount of hydrogen reacting with the oxidizer).

Among cryogenic components of rocket propellants, liquid hydrogen is practically the only one that can be used to cool the combustion chamber. This is due to the high heat capacity and thermal conductivity of the gaseous hydrogen interlayer formed during the film regime of boiling at the hot wall (an interlayer of other gases sharply decreases the heat transfer from wall to liquid). Hydrogen is characterized by an extremely high penetrability and requires special

steps to seal welds, joints and even solid sheet materials. The escape of the gas and its explosiveness can be reduced by using two-phase solid-liquid hydrogen. Hydrogen slush, containing one-half or more of the solid phase in the form of particles 1-5 mm in size, is obtained by cooling liquid hydrogen to the crystallization temperature, which is 7° below the boiling point, by removing the heat of vaporization by prolonged evacuation (several hours) of the gas above the liquid with a vacuum pump. The density of the liquid phase in the slush is 0.0771 (almost 10% higher than at the boiling point), and the density of solid hydrogen is 0.0868 (22% higher).

Oxygen-hydrogen fuel requires forced ignition; one of the ways of achieving it is by using chemical kindling. Two ignition fuels that can be used are trimethylaluminum $\text{Al}(\text{CH}_3)_3$ or triethylaluminum $\text{Al}(\text{C}_2\text{H}_5)_3$, which self-ignite on contact with oxygen (it must be kept in mind that they also self-ignite in air); another ignition oxidizer that can be used is chlorine trifluoride ClF_3 , which self-ignites on contact with hydrogen [5, 15, 54, 68, 73, 86, 109, 125, 134, 137, 140].

LIQUID MONOPROPELLANTS

General Description

Monopropellants may also be liquids whose decomposition involves the liberation of thermal energy and total gasification (Table 11), as well as stable solutions of fuel in oxidizer. Because of the danger of their detonation, the substances used in practice have moderate energy characteristics; their use as propellants for primary liquid propellant engines of rockets and airplanes is

considered inadvisable. However, they may be advantageous in steering and other auxiliary engines of spacecraft, operating for short periods of time or in bursts, since they permit a simple and easily operated propellant feeding system and do not require cooling of the combustion chambers. In addition, they are used as auxiliary propellants triggering the turbopump assembly of the basic LRE [55, 73, 86].

1. Топливо	2. Химическая формула	3. Плотность при 20°С	4. Температура плавления, °С	5. Температура кипения, °С	6. Теплота разложения, ккал/кг	7. Температура сгорания, °С	8. Удельная тяга (при $p_c = 68$ абсолютных атмосфер), кг-сек/кг
9. Перекись водорода (100%)	H_2O_2	1,448	-1	150	380	1000	165
10. Перекись водорода (87%)	H_2O_2	1,381	-13	142	250	660	126
11. Гидразин	N_2H_4	1,008	+2	114	380	630	198
12. Нитрометан	CH_3NO_2	1,137	-28	+101	—	2370	254
13. Окись этилена	C_2H_4O	0,869	-111	+11	600	1000	199

Table 11. Characteristics of Liquid Monopropellants. Key:

1. Propellant; 2. Chemical formula; 3. Density at 20°C; 4. Melting point, °C; 5. Boiling point, °C; 6. Heat of decomposition, kcal/kg; 7. Combustion temperature, °C; 8. Specific thrust (at $p_c = 68$ absolute atmospheres), kg sec/kg; 9. Hydrogen peroxide (100%); 10. Hydrogen peroxide (87%); 11. Hydrazine; 12. Nitromethane; 13. Ethylene oxide.

Hydrogen Peroxide

The decomposition of 100% peroxide $H_2O_2 \rightarrow H_2O + 1/2 O_2$ may take place as a result of random, uncontrollable causes, and therefore hydrogen peroxide of 80-95% concentration containing a stabilizer is usually employed. The effect of the concentration of hydroperoxide on its physical and energetic properties is shown in Fig. 32. With water, it forms the compound $H_2O_2 \cdot 2H_2O$ (48.6% hydrogen peroxide), which freezes at -51°C; the 43-60% concentration range has the character of eutectic solutions. Compositions with a relatively high freezing point tend toward

supercooling by 20°-30°C. The heat evolved by the decomposition of the peroxide in the region of its complete transformation into steam and gas (above 62% concentration) is determined from the equation

$$H = [H_2O_2] \cdot 380 - [H_2O] \cdot 600 \text{ kcal/kg} \quad (5.10)$$

where the weight fraction of the corresponding substance is enclosed in square brackets. In the steam generator of LRE, the decomposition of hydrogen peroxide takes place under the influence of solid or liquid catalysts - silver wire, sodium permanganate solution, and metal oxides.

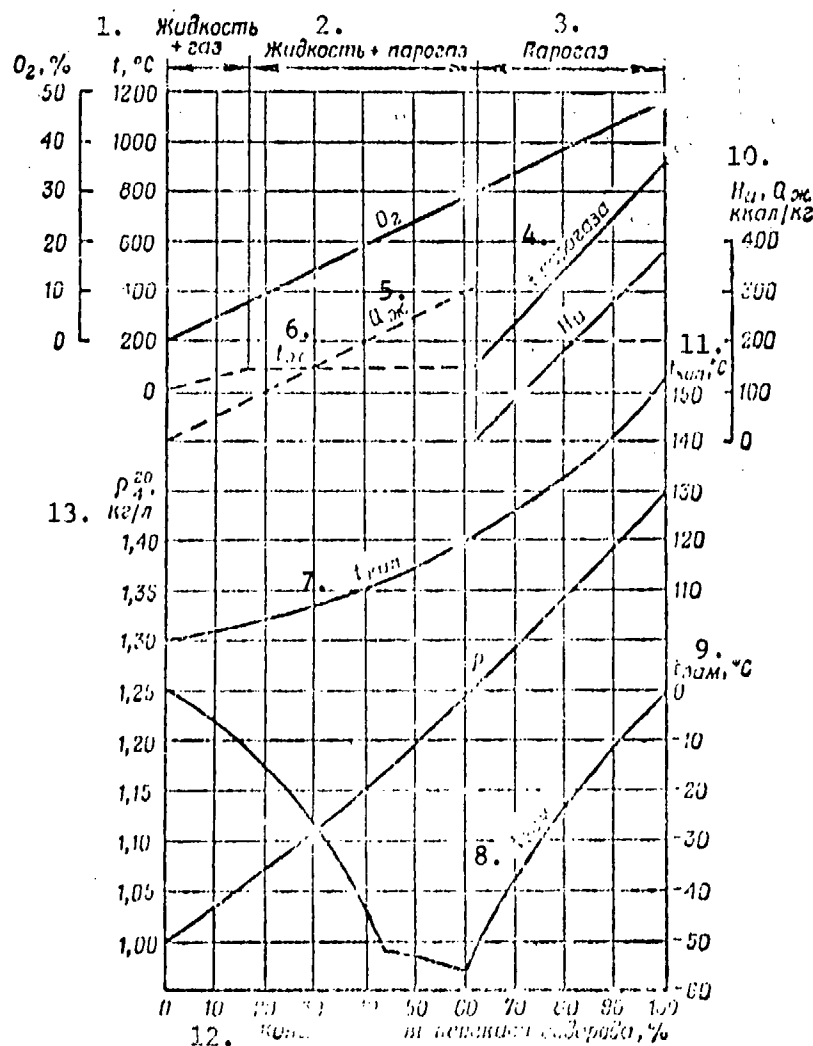


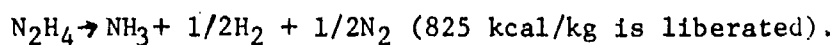
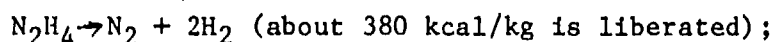
Fig. 32. Effect of concentration of hydrogen peroxide on its physical properties (density ρ , boiling point t_b and freezing point t_f), on the calorific value H_u and vapor-gas temperature t_{vg} , on the heat of decomposition Q_d and temperature t_d up to complete decomposition to vapor-gas and on the amount of free oxygen O_2 evolved by the decomposition; the state following decomposition is indicated at the top. Key:

1. Liquid + gas; 2. Liquid + vapor-gas; 3. Vapor-gas; 4. t of vapor-gas; 5. Q_d ; 6. t_d ; 7. t_b ; 8. t_f ; 9. t_f , °C; 10. H_u , Q_d kcal/kg; 11. t_b , °C; 12. Hydrogen peroxide concentration, %; 13. kg/l

In the American rockets Redstone and Jupiter, concentrated hydrogen peroxide is an auxiliary propellant for turbopump assemblies. Various hydrogen peroxide engines of small thrust have been developed abroad, including an individual back-pack motor for an astronaut's movements in open space. Concentrated peroxide contains a considerable quantity of active oxygen, but is seldom used as the oxidizer of basic rocket fuel, since it is less effective and more dangerous in handling than nitric acid and liquid oxygen [15, 55, 73].

Characteristics of Certain Propellants

Hydrazine can be used as a monopropellant, since it decomposes into hydrogen, nitrogen and ammonia with evolution of heat:



The second reaction takes place only at low temperatures; the higher the temperature, the more ammonia decomposes into nitrogen and hydrogen. Aluminum oxide impregnated with iridium is used as the decomposition catalyst. Hydrazine is used in many American LRE with thrusts ranging from tens of grams to hundreds of kilograms, designed for the control and maneuvering of spacecraft.

The molecular composition of nitromethane CH_3NO_2 and propyl nitrate $\text{C}_3\text{H}_7\text{ONO}_2$ contains combustible elements (C, H) and an oxidizing element (O) that have not reacted chemically with one another: they are separated by a nitrogen barrier. Decomposition involves an oxidation process that yields a large exothermic effect. To eliminate the danger of explosion and coke formation, additives are added to these compounds.

Ethylene oxide $\text{H}_2\text{C} \begin{array}{c} \diagup \text{O} \diagdown \end{array} \text{CH}_2$ decomposes with the formation of a mixture of carbon monoxide CO , methane CH_4 , ethylene C_2H_4 , and hydrogen H_2 . It is accessible and cheap, since it is widely used in the organic synthesis industry, and is comparatively safe in handling [29, 86, 121].

CHARACTERISTICS OF HANDLING OF LIQUID ROCKET PROPELLANTS

Choice of Materials and Measures Against Corrosion

Nitrogen oxidizers and concentrated hydrogen peroxide corrode almost all materials and carbonize ordinary lining materials, hoses and tubing made of natural textile materials and rubber. Tanks for nitric acid and hydrogen are usually made of pure aluminum, and various pumps and the propellant equipment of the engine are made of acid-resistant high-alloy chromium-nickel steel. In the presence of corrosion inhibitors, which form a protective film of insoluble salts, they are not attacked by concentrated acid. The action of an involatile inhibitor, for example phosphoric acid H_3PO_4 , is considered effective in the liquid phase, and that of a volatile inhibitor, in particular, hydrogen fluoride HF , in the vapor phase above the propellant level. The inhibitor corrodes glass.

Water-diluted nitric acid also attacks pure aluminum, since dilution of the acid increases the degree of dissociation of its molecules and the rate of electrochemical corrosion processes. When hydrogen peroxide is diluted with water, its corrosiveness decreases.

Acid-resistant plastics (for example, polymers of fluorinated hydrocarbons) and asbestos are used as lining and sealing materials and coatings in connection

with nitric acid and hydrogen peroxide. For hoses and tubings, chemically stable elastic plastics such as polychlorovinyl, etc. may be used.

Hydrazine, ammonia and their derivatives, which have alkaline properties, corrode copper and copper alloys. For this reason, these alloys usually are not used in equipment designed to run on these fuels. To avoid destruction by amines, ordinary lining and textile materials are subjected to special impregnation, or amine-resistant plastics are employed.

Cryogenic components are practically safe from the standpoint of corrosion of metals. However, at temperatures of minus 150-250°C, almost all steels, as well as rubber and many plastics, become brittle. Satisfactory mechanical properties at these temperatures are those of aluminum and copper alloys and chromium-nickel austenitic steels; they are used in the manufacture of tanks and equipment for cryogenic components. Evacuated jackets, vacuum-powder insulation, foam plastics, slag wool, etc., are used for thermal protection. To avoid losses and the formation of vapor lock in the propellant supply lines, as well as thermal deformation during fueling with cryogenic components, the entire propellant system is first cooled down [67]. The fueling is carried out shortly before takeoff so as to avoid the formation of frost on the outside of the vehicle [6, 86, 90].

Explosion Hazard and Stability

The explosion hazard of rocket propellants is related to their instability and contamination with substances which may react chemically with the components or act as catalysts of their decomposition. The most explosive are monopropellants, in particular, hydrogen peroxide. Almost all substances other than pure aluminum,

stainless steel and certain plastics promote hydrogen peroxide decomposition, which develops with self-acceleration and ends in an explosion when the temperature reaches 175°C. For this reason, when working with hydrogen peroxide, use is made of equipment made from suitable materials, and close attention is given to the purity of both the peroxide itself and the surfaces coming in contact with it. The surfaces are subjected to so-called passivation by treating them with substances forming an inactive film. The compressed gases used in work with hydrogen peroxide are filtered by removing dust and other impurities. Incipient hydrogen peroxide decomposition is manifested in an increased evolution of gas through the vent and a rise in the peroxide temperature above the temperature of ambient air. To prevent an explosion, hydrogen peroxide is usually diluted with a considerable amount of water, whereupon it becomes unsuitable as a propellant. The explosion hazard of certain monopropellants and oxidizers, for example nitromethane CH_3NO_2 , tetranitromethane $\text{C}(\text{NO}_2)_4$, and ozone O_3 , is the main reason for the lack of their practical application.

The danger of an explosion arises when water reaches the nitric acid oxidizer, since this evolves a large quantity of heat and there is an abundant formation of steam. An explosion may result from the condensation and crystallization in cryogenic propellants of chemically reactive substances whose accumulation at a certain concentration causes a vigorous reaction: oil (from pumps) and acetylene (from air) in liquid oxygen, oxygen in liquid hydrogen, etc. Explosive self-ignition takes place on contact between oxygen and certain organic compounds such as fats, oils, etc: work with oxygen makes it necessary to keep the containers and propellant equipment scrupulously clean.

A very explosive gas is oxyhydrogen gas $\text{H}_2 + \text{O}_2$ in the case of accumulation of evaporated hydrogen in a mixture with air. However, hydrogen poured in a large

amount and ignited burns quietly at the surface without explosions, and its flame, because of the high combustion rate, is insensitive to wind [26, 73, 90].

The explosive force of rocket propellants with high-energy characteristics is very great [122]. According to experimental data, the diameter of the fire ball instantaneously formed by the explosion $d \approx 3.9 \sqrt[3]{G_p}$ [m], and the duration of action of the explosive $\tau \approx 0.26 \sqrt[3]{G_p}$ [sec] (where G_p is the weight of propellant in kg). In the case of an explosion of a rocket such as Saturn V, this gives a fire ball diameter of about 400 m, and the duration of action of the explosion is around 30 sec.

Fire Safety Measures

The majority of fuels employed in rocketry do not differ very much from gasolines and kerosenes in fire hazard characteristics. However, tanks and fueling devices containing fuels which self-ignite in contact with nitrogen oxidizers (dimethylhydrazine, tonka, etc.) are placed at a considerable distance from them. Nitrogen oxidizers and hydrogen peroxide cause the self-ignition of wood, fabrics, dry leaves, grass, etc. To prevent fires, the surfaces and floors of areas where work with these oxidizers is being carried out are covered with acid-resistant concrete (not asphalt), and the bodies of trucks are provided with acid-resistant metal oil pans.

In the vicinity of liquid oxygen tanks, the air contains more gaseous oxygen than usual, and the fire hazard presented by any external flame source is therefore greater. Oxygen is absorbed by cotton fabrics and is retained by hair (including eyebrows and eyelashes). After exposure to an atmosphere with an increased oxygen content, one must not smoke or come near an open fire.

The principles and means of extinguishing the fuel components of rocket propellants are the same as for ordinary petroleum fuels: they are quenched with carbon dioxide foam extinguishers or chemical quenching liquids, but not with water. In contrast, a fire caused by liquid oxidizers is usually quenched only by using water: the latter dilutes the oxidizer, decreases its reactivity, and sharply cools the combustion kernel. Substances usually employed in quenching fuels are useless in this case, since their action is chiefly based on isolating the combustion kernel from access of atmospheric oxygen, and in the presence of nitric acid or hydrogen peroxide, no access of air is required for the combustion. Ordinary quenching agents for small flame kernels such as asbestos blankets, felting, etc. cannot be of any assistance either [73, 86, 90].

Toxicity

Many rocket propellants either are lethal poisons or cause serious injury to the organism. Nitric acid, nitrogen oxides, or concentrated hydrogen peroxide cause serious burns when they come in contact with the skin. Particularly serious injuries to live tissue which do not heal for a long time are caused by nitric acid. Gaseous nitrogen oxides and nitric acid vapor cause acute irritation of the respiratory tract and lungs and attack the cornea of the eye and teeth. Being blood poisons, they have a general poisoning effect on the organism. A high oxygen concentration causes pneumonia. Hydrazine and EDMH are basically blood poisons. UDMH is approximately twice as toxic as nitric acid. When it accumulates in the organism, it attacks the lungs, liver, and kidneys. Amines attack the central nervous system and blood. Heavy poisoning with amines results in the loss of consciousness, paralysis, and death. The direct action of amines on the skin is insignificant, but they are capable of penetrating through it into the organism. Chronic poisoning with amines leads to skin disease.

The initial symptoms of poisoning in many cases include dizziness, nausea and vomiting, heavy cough, weakness, psychic excitation, cyanosis (fingers, lips, and tips of the ears turn blue). The symptoms of poisoning do not always appear immediately; they sometimes disappear rapidly, but a few hours later, the poisoning manifests itself with full force [20, 73, 84, 86, 90].

SPECIAL PROPERTIES OF SOLID ROCKET PROPELLANTS AND THEIR QUALITY REQUIREMENTS

Types of Solid Propellants

According to their physicochemical nature, solid rocket propellants are divided into two groups: composite propellants (mixtures of fuels with oxidizers) and double-base propellants. (Colloidal systems of nitrocellulose and nitroglycerine). According to their uses, solid propellants may be divided into working propellants and ignition compositions; the latter are usually classified as composite propellants from the standpoint of their physicochemical nature [55, 73, 91].

Rate of Combustion

The combustion of a solid rocket propellant takes place at the surface in parallel layers. Actually, what burns is not the solid substance itself, but the products of its gasification: the flame front (luminous zone) is established at a distance of the order of a tenth of a millimeter from the surface of the propellant charge. The heat flux from the flame heats a thin surface layer of propellant and therein induces reactions of decomposition, partial oxidation, and others, associated with foaming, melting, vaporization, and smoking. The displacement rate of the open surface of solid propellant along the normal (in other

words, the thickness of the layer of propellant burning per second is called the linear combustion rate (w_c). Its magnitude ranges from a few millimeters to several centimeters per second. It also depends on the chemical reactivity of the propellant, on the heat transfer of the flame, and also on the temperature capable of causing gasification of a given propellant composition (fusion and vaporization or decomposition): the higher this temperature, the closer the flame is to the surface, and the faster the combustion rate. The microstructure of the propellant is also important: the oxidizer grain size in the composite propellant determines the surface of contact with the fuel along which the reactions take place in the heating zone (Fig. 33, dashed curves) and the amounts of added catalysts (salts, hydrides), retardants (for example, paraffin), pigments (usually, carbon black promoting absorption of heat radiation), and high-melting metals (tungsten, etc.).

The required linear combustion rate is related to the specific use, size and design of the propellant charges. For accelerating engines, accelerators operating for short periods of time and starting charges, fast-burning propellants are required, and for sustainer motors and solid-propellant gas generators, slow-burning propellants are desirable [28, 55, 73, 86, 111].

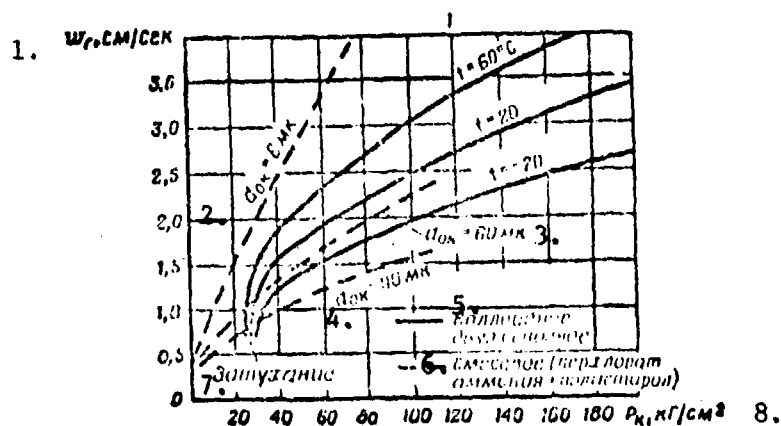


Fig. 33. Effect of propellant temperature and particle size of ingredients on the dependence of combustion rate w_c on chamber pressure p_c for two propellants. Key:

1. $w_c, \text{cm/sec}$; 2. $d_{ox} = 6\mu$
3. $d_{ox} = 60\mu$; 4. $d_{ox} = 110\mu$
5. Colloidal double-base propellant;
6. Composite propellant (ammonium perchlorate + polystyrene);
7. Extinction; 8. $p_c, \text{kg/cm}^2$

Sensitivity to Pressure and Temperature

The chief requirement imposed on a solid rocket propellant and related to the characteristics of its combustion is the slightest possible dependence of the combustion rate on the pressure in the chamber (p_c) and on the initial temperature of the propellant (t_p). Their influence is usually expressed in the form of a dependence called the law of V'yel':

$$w_{co} = k_t p_c^n \quad (5.11)$$

where the exponent $n \approx 0.1$ to 0.8 (called the combustion index), and the quantity k_t , which characterizes the influence of the propellant temperature on the combustion rate, is a function of the temperature coefficient $\epsilon \approx 0.001$ to 0.007 ;

$$k_t = k_{t_0} + \epsilon (t_p - t_0). \quad (5.12)$$

Lower values $n \approx 0.1$ to 0.5 and $\epsilon \approx 0.001$ to 0.003 characterize composite propellants, and higher values, $n \approx 0.7$ to 0.8 and $\epsilon \approx 0.005$ to 0.007 , are typical of double-base propellants. Propellants having little sensitivity to pressure (with a low combustion index n) provide for a higher stability of engine operation and smaller fluctuations of pressure and thrust. Completely inadmissible is $n \approx 1$; fuel with such a combustion index would cause an explosion of the engine upon any random increase in pressure, or extinction if the pressure was lowered.

The higher the initial temperature of the propellants, the more intensive its decomposition and higher the combustion rate, gas formation per second, and pressure in the combustion chamber. A 1°C rise in propellant temperature causes a pressure increase of approximately 1.2% for double-base propellants and 0.5% for

composite ones. When propellants of little sensitivity to temperature are used, it is simpler to achieve the required engine operating conditions and a smaller dispersal when the rockets are used in combat. If the chamber pressure is below 20-26 atmospheres, decomposition of the propellant slows down, and combustion either becomes intermittent (the engine makes a popping sound) or ceases altogether. The lower the propellant temperature, the higher the pressure necessary for starting for stable combustion (see the extinction zone in Fig. 33). Double-base propellants are also inferior to composite ones in this index.

An excessively high chemical reactivity and calorific value of a solid propellant may give rise to conditions promoting knocking in the presence of a sharp pressure and temperature differential, for example, in the presence of a strong shock, an intense electrical discharge, etc. In order to preclude this possibility, a "rich" composition of high-energy propellants is chosen in advance ($\alpha < 1$) [5, 28, 55, 111].

Mechanical Properties

During storage, transportation, and flight, the geometry of the charge must not change, since an unanticipated increase in combustion surface area leads at best to a change in the engine setting and flight program, and at worst, to an explosion or engine shutdown. For this reason, a solid rocket propellant should have desirable mechanical properties, i.e., a high strength, impact strength and elasticity at both high and low temperatures, so that a high pressure, inertial overloads and thermal deformation do not cause cracks or destruction of the charge. The propellant should constitute, not a loose, but a continuous mass without pores or microchannels along which hot gases could penetrate into the interior and cause uncontrollable decomposition and combustion processes. A propellant

for large-sized charges must not have any tendency to creep or shrink, and should be characterized by surface adhesion to the material of the chamber casing and to the noncombustible coating (inhibitor), which shapes the working portions of the charge [5, 55, 86].

Importance of Density

Among the requirements placed on all rocket propellants, and especially important one for solid propellants is a high density. This is due to the fact that solid propellants have lower specific thrusts than liquid propellants, and the reserve of solid propellant is limited by the space in the engine combustion chamber. The actual density of solid propellants may exceed the calculated density of liquid bipropellants by a factor of 1.5-2 or more, which makes it possible to provide a thrust impulse equal to that of a liquid propellant [5, 73, 91].

COMPOSITE SOLID ROCKET PROPELLANTS

General Description

Composite rocket propellants (also called heterogeneous) are mechanical mixtures of crystalline oxidizer (65-80%) with a polymer fuel (10-20%) which simultaneously acts as a binder holding the mass of fine particles of oxidizer together and imparting the necessary mechanical properties to the solid propellant. In addition, they usually contain 5-15% of a metal, which increases the calorific value, and up to 10% of additives. In energetic properties, combustion characteristics, and possibility of forming large-sized charges, composite propellants are better than

double-base (colloidal) propellants. These qualities ensure a steadily expanding role of composite propellants in rocketry [5, 55, 73, 91, 111].

Solid Oxidizers

The oxidizers in the composition of composite propellants are oxygen-containing salts of perchloric acids - ammonium or potassium perchlorates and ammonium, potassium or sodium nitrates (Table 12). The total oxygen content in perchlorates is lower than in the corresponding nitrates (64.3% in the residue of perchloric acid, ClO_4 , and 77.4% in the residue of nitric acid, NO_3). However, the metal of perchlorates or part of the hydrogen of the NH_4 group is bound to chlorine, so that more fuel can be oxidized. The decomposition products of ammonium salts are gaseous, and the metal-containing perchlorates and nitrates form a certain amount of solid (smoke) particles of chlorides (NaCl , KCl) or oxides of metals (Na_2O_2 , K_2O_2 , etc.), which decrease the gas formation and specific thrust. The radiation of the solid particles increases the heating of the combustion chamber and nozzle, and their mechanical action erodes the nozzle walls. However, the metal salts have a higher density.

In overall properties, one of the best oxidizers in the composition of solid propellants is ammonium perchlorate NH_4ClO_4 . It decomposes at a relatively low temperature, 200-450°C (without melting first), so that propellants based on it have a moderate linear combustion rate which is most advantageous in the majority of cases. Owing to the presence of hydrogen, it increases the calorific value of the propellant, and a significant portion of its decomposition products is constituted by water vapor and nitrogen, which are characterized by a comparatively high specific volume (gas formation). For this reason, despite their

moderate content of active oxygen, propellants based on ammonium perchlorate are characterized by desirable energetic indices. Ammonium perchlorate has a slight hygroscopicity. Its negative qualities include an insufficient stability, tendency to detonate at high pressures and temperatures, and formation of hydrochloric acid fog when the combustion products escape into a humid atmosphere. Potassium perchlorate $KClO_4$, despite its high content of active oxygen, yields a 15-20% lower specific thrust owing to the consumption of heat by the decomposition and to the formation of solid KCl particles. Its use makes it possible to obtain desirable mechanical properties of the charge more easily, since a larger quantity of fuel binder can be introduced into the propellant. Lithium perchlorate $LiClO_4$ is being studied; it yields even more oxygen to oxidize the fuel, is stable, and is safe in handling.

Nitrates, i.e., ammonium, sodium and potassium nitrates, are cheap, readily available oxidizers (they are widely employed in agriculture as fertilizers). They are less effective than perchlorates and are hygroscopic, this being reflected in the mechanical properties of the propellant. A serious drawback of ammonium nitrate is the change in its crystal structure with changing temperature, associated with a change in volume and the formation of cracks in the charge [25, 29, 73, 86].

Fuel Binders

The fuel and simultaneously the binder in the composition of composite solid propellants are various synthetic polymers of rubber, resin, and plastic types (Tables 1 and 3). The most widely used are polyurethane $(NH \cdot COO \cdot C_{nH_m})_x$ - a rubber-like polymer with comparatively low energetic characteristics but good mechanical

properties, including cold resistance and adhesion providing a strong bond between the charge and the combustion chamber wall. In extended storage, however, a gradual deterioration of its mechanical properties takes place. Butadiene rubber $(C_4H_6)_x$ and butadiene-styrene rubber $(C_4H_6 \cdot C_2H_3 \cdot C_6H_5)_x$ have better energetic properties than polyurethane, but because of a high stoichiometric coefficient, they are not introduced in the amount that ensures the required mechanical properties of the propellant. Polysulfide rubber $(C_2H_4-O-C_2H_4-S_4)_x$, or thiokol, which contains a substantial amount of ballast sulfur, has poorer energetic properties, but a low stoichiometric coefficient. This permits its introduction in large quantity into the composition of composite propellants. Imparting good mechanical properties to the propellant at positive temperatures, it becomes brittle at subzero temperatures ($-15^\circ C$). Very strong, but rather inelastic charges, brittle at low temperatures, are obtained when epoxy or phenol formaldehyde resin is used as the fuel binder. A special type of fuel binder is nitrosol (gelatinized nitrocellulose), which contains a significant quantity of active oxygen (corresponding to $\alpha \approx 0.6$). Its combustion requires less oxidizer than that of nonoxygen fuels. The required mechanical properties of the charge are thus more easily obtained [73, 86, 91, 111].

1.	2.	3.		6.	7.	8.	9.	10.	11.
		Элементный состав, кг/кг							
Окислитель	Молекулярная масса	4.	5.						
		Кислорода [O] _{ок}	Водорода [H] _{ок} , металлов [Me] _{ок}	Содержание активного кислорода [O] _{акт}	Потребное количество кислорода по отношению к кислороду	Полная энтальпия H _{ок} , ккал/кг	Тепловой эффект H _{ок} , ккал/кг	Плотность, г/см ³	Температура плавления, °C
12. Перхлораты:									
NH ₄ ClO ₄	117,50	0,516	0,251 ¹	0,343	2,92	-600	+340	1,95	270 ³
KClO ₄	138,56	0,462	0,282	0,462	2,17	-740	-150	2,53	525
HClO ₄	106,40	0,602	0,065	0,632	1,66	-860	+240	2,43	247
13. Нитраты:									
NH ₄ NO ₃	80,50	0,599	0,050	0,202	4,95	-1090	-320	1,73	170
KNO ₃	101,11	0,474	0,387	0,316 ²	3,16	-1165	-750	2,11	333
NaNO ₃	85,01	0,565	0,258	0,376 ²	2,79	-1310	-700	2,26	310

14. ¹Не связываемый хлором.
15. ²Не связываемый металлом.
16. ³Температура разложения.

Table 12. Composition and certain properties of solid oxidizers [86]. Key:

1. Oxidizer; 2. Molecular weight; 3. Elemental composition, kg/kg; 4. Oxygen [O]_{ox}; 5. Hydrogen [H]_{ox}, metal: [Me]_{ox}; 6. Active oxygen content [O]_{act}; 7. Required amount in relation to oxygen; 8. Total enthalpy I_{ox}, kcal/kg; 9. Energy release of H_{ox}, kcal/kg; 10. Density, g/cm³; 11. Melting point, °C; 12. Perchlorates; 13. Nitrates; 14. ¹Not bound to chlorine; 15. ²Not bound to metal; 16. ³Decomposition temperature.

Addition of Metals

The energetic indices of a composite propellant can be increased by adding aluminum or other metals. Their combustion requires little oxidizer, so that per unit weight, they yield 2-2.5 times as much heat as polymers. Introduction of metals into the latter deprives them of only a slight portion of oxidizer. The heat liberated by the combustion of metals is transferred to the gaseous combustion products of the main propellant mass, raising the gas temperature and specific thrust of the engine. The combustion products of the metals are formed as condensed particles (smoke, not gas), causing specific thrust losses. There

exists a certain optimum content of metals in the propellant (of the order of 10-20%) providing for the maximum specific thrust; it is difficult to achieve, however, because the metal as well as the oxidizer requires a binder. The more polymeric fuel binder is present in the propellant composition, the more metallic fuel can be introduced into it while retaining the satisfactory mechanical properties of the propellant. For this reason, composite propellants are usually highly enriched with the fuel, approximately up to $\chi = 0.5-0.6$ (Fig. 34). Certain properties of metals as fuels are listed in Table 13.

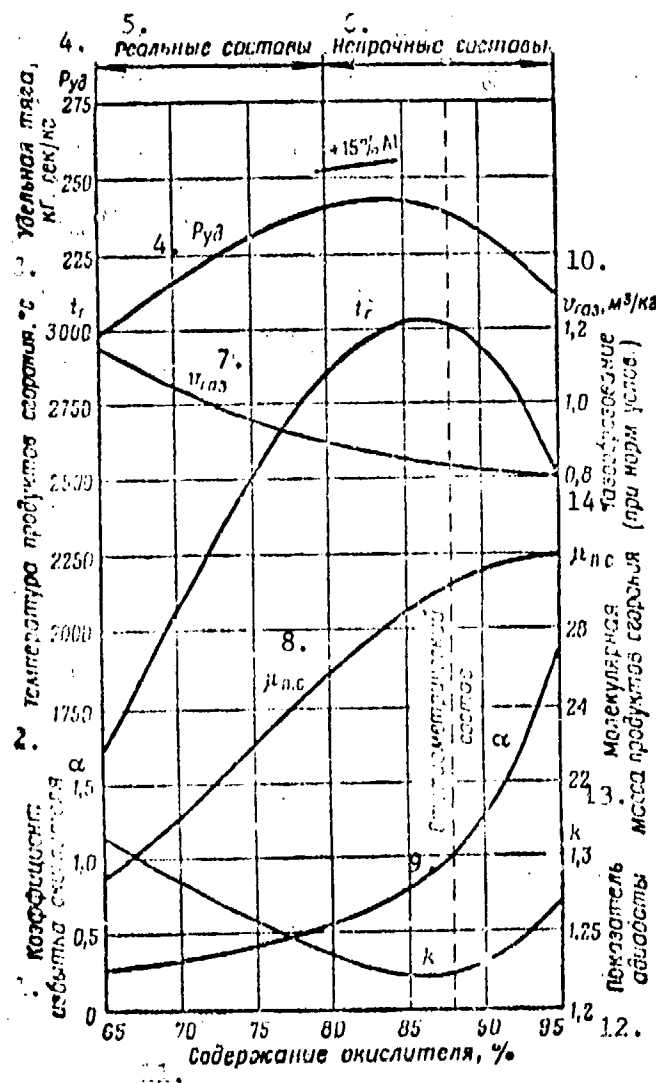


Fig. 34. Calculated characteristics of composite solid propellant (ammonium perchlorate + polyester) of various compositions ($p_c = 70 \text{ kg/cm}^2$); the effect of aluminum additive on the specific thrust is indicated at the top. Key:

1. Excess oxidizer coefficient;
2. Temperature of combustion product, $^{\circ}\text{C}$;
3. Specific thrust, kg sec/kg ;
4. P_{cp} ;
5. Actual compositions;
6. Weak compositions;
7. V_{gas} ;
8. λ_{cp} ;
9. Stoichiometric composition;
10. $V_{gas}, \text{m}^3/\text{kg}$;
11. Oxidizer content, %;
12. Specific heat ratio;
13. Molecular weight of combustion products;
14. Gas formation (at standard conditions)

The metal is most frequently introduced into the propellant composition in the form of a finely divided powder (1-2%). To increase the strength of the charge, use may be made of reinforcing structural elements made of metal, such as fine wire, screen, fiber, foil (including a honeycomb foil framework). The metal combustion efficiency is poorer in this case.

The great natural reserves and large scale of world production of aluminum permit its use as a fuel to a greater degree than any other metal. In calorific value it is inferior to beryllium and lithium; this is compensated to some extent by its higher density. Aluminum powder increases the stability of propellant combustion. To provide protection from oxidation, its particles are passivated in the course of preparation (for example, by a condensation film of organic compounds). Beryllium is a rare and comparatively expensive metal; it is second to hydrogen in heat of combustion among all the chemical elements, and when introduced into a propellant, it catalyzes the solidification of the polymer fuel. Magnesium is lighter than aluminum and beryllium, its calorific value is low, but because of a small stoichiometric coefficient, it evolves more heat per unit weight of oxygen than any other fuel. Magnesium accelerates the propellant combustion rate. The natural world resources and scale of its production are extensive. Lithium surpasses aluminum and magnesium in the amount of heat evolved per unit weight of mixture with the oxidizer, but because of its low density, is considerably inferior not only to metallic fuels but also to polymeric ones in volume calorific value. The natural reserves of lithium are considerable, but its world production scale is still small.

1. Наименование показателей	2. Алюминий	3. Бериллий	4. Литий	5. Магний	6. Бор
7. Теплотворность горючего, kcal/kg	7400	15900	10300	5930	14000
8. Стохиометрический коэффициент по кислороду (требуемое количество кислорода), kg/kg	0,89	1,78	1,15	0,66	2,22
9. Теплотворность стехиометрической смеси с кислородом, kcal/kg	3920	5720	4780	3590	4330
10. Плотность металла, g/cm^3	2,70	1,85	0,534	1,74	2,30
11. Энергоемкость металла, kcal/l	10800	19400	3500	10300	52200
12. Температура плавления металла, $^{\circ}\text{C}$	660	1284	180	651	2027
13. Температура кипения металла, $^{\circ}\text{C}$	2467	2484	1347	1108	3677
14. Состав окиси металла	Al_2O_3	BeO	Li_2O	MgO	B_2O_3
15. Температура плавления окиси, $^{\circ}\text{C}$	2050	2550	1450	2800	450
16. Температура кипения окиси, $^{\circ}\text{C}$	2700	3900	1700	3000	2925
17. Теплота конденсации окиси, kcal/kg	3300	18000	7400	6100	4800

Table 10. Energetic and physical properties of metallic fuels and boron [29, 86]. Key:

1. Index; 2. Aluminum; 3. Beryllium; 4. Lithium; 5. Magnesium; 6. Boron; 7. Calorific value of fuel, kcal/kg ; 8. Oxygen stoichiometric coefficient (required amount of oxygen), kg/kg ; 9. Calorific value of stoichiometric mixture with oxygen, kcal/kg ; 10. Density of metal, g/cm^3 ; 11. Energy capacity of metal, kcal/l ; 12. Melting point of metal, $^{\circ}\text{C}$; 13. Boiling point of metal, $^{\circ}\text{C}$; 14. Composition of metal oxide; 15. Melting point of oxide, $^{\circ}\text{C}$; 16. Boiling point of oxide, $^{\circ}\text{C}$; 17. Heat of condensation of oxide, kcal/kg .

In addition to metals, boron is also added; it is an amorphous or crystalline substance of dark brown or black color with a high calorific value. In contrast to the metals discussed above, it requires a relatively large amount of oxidizer; this hinders its use in the composition of solid propellants. Better properties, including a higher combustion efficiency, are exhibited by the solid boron hydride decaborane, $\text{B}_{10}\text{H}_{14}$. Its calorific value (higher than that of boron) is 15,600 kcal/kg , its density 0.92, and its melting point, 219°C . Its disadvantage is its hygroscopicity [5, 73, 86, 111].

Ignition Propellant

The ignition compositions used are composite propellants giving a large quantity of smoky combustion products: potassium perchlorate with magnesium or aluminum powder, and also black powder, i.e., a mixture of potassium nitrate, wood charcoal, and sulfur. The radiation of smoke particles provides for a rapid heating up of the surface of the working solid propellant during the starting of SPRE. The powder has a poorer emissivity, but does not oxidize during storage and is therefore reliable [24].

DOUBLE-BASE (COLLOIDAL) SOLID ROCKET PROPELLANTS

Physicochemical Nature

Double-base or colloidal solid propellants (also called homogeneous propellants and ballistic powders) have two characteristic features. First, they have a colloidal microstructure, the two bases of which are solid nitrocellulose (which however is loose in the initial state), and a solvent, nitroglycerin (sometimes dinitrotoluene, etc.), which binds it into a continuous solid mass. Second, their molecules simultaneously contain the fuel hydrocarbon part and the oxygen ready to react with it, separated from the fuel elements by a "barrier" of nitrogen atoms (of the NO_2 group). On heating or impact, the "barrier" is broken, the nitrogen atoms combine into gaseous N_2 molecules, and the liberated oxygen atoms vigorously react with atoms of the fuel elements - hydrogen and carbon: combustion thus takes place. The microinhomogeneity of the colloidal structure of the propellant in this case prevents an explosion, a tendency toward which is manifested by each of the initial component parts taken separately. Pure nitrocellulose

explodes because of the enormous surface area of the loose porous substance over which the combustion spreads, while nitroglycerin detonates on impact [25, 73, 91, 103, 111].

Nitrocellulose

The nitrate esters obtained by treating cellulose (cotton, cotton fluff, or fibrous wood cellulose) with nitric acid consist of polymer chains of several hundred or thousand units $C_7H_6O_2(OH)_n(ON_2)_{3-n}$, where $n \leq 3$. In the units of the polymer chain, the number of ON_2 groups may be different, and therefore the degree of nitration of cellulose is characterized, not by its chemical formula, but by the nitrogen content. In nitrocellulose used for rocket propellants, the nitrogen content is 12-13%; the active oxygen content is 2.86 times as high as the nitrogen content.

Nitrocellulose does not contain enough oxygen to convert the entire carbon and hydrogen into the oxidation end products ($\lambda < 1$). The higher the degree of nitration, the more carbon and hydrogen are oxidized, and the higher the calorific value of the propellant. However, increasing the degree of nitration worsens the solubility of nitrocellulose in nitroglycerin and increases its hygroscopicity (the amount of moisture absorbed from the air may reach 2%) [23, 24, 33, 73, 11].

Nitroglycerin

In pure form, nitroglycerin $C_3H_5(ONO_2)_3$ is a thick, oily liquid, colorless or slightly yellow, one of the most powerful and dangerous explosives. Its

calorific value is approximately 1.5 times that of nitrocellulose. Nitroglycerin contains excess oxygen ($\lambda = 1.06$) which during the combustion of a double-base propellant is consumed in the oxidation of the combustible elements of nitrocellulose. The stoichiometric composition of the double-base propellant ($\lambda = 1$) is 89.5% of nitroglycerin and 10.5% of nitrocellulose, but because of dissociation of the gases, the maximum specific thrust is obtained at 50% of nitroglycerin. However, a propellant containing more than 43.5% of nitroglycerin is unsuitable from the standpoint of strength and stability: it demixes into layers with the separation of liquid nitroglycerin [23, 24, 30].

Additives

Into a double-base propellant, up to 10% of the following additives are introduced: centralite (diethyldiphenylcarbamide) $\text{CO}(\text{N} \cdot \text{C}_6\text{H}_5 \cdot \text{C}_2\text{H}_5)_2$ and diphenylamine $\text{NH}(\text{C}_6\text{H}_5)_2$ to stabilize the propellant, oil or vaseline to facilitate extrusion, carbon black to prevent heating of the charge by radiation, diethyl phthalate to protect it from moisture, etc.

The technology of manufacture of solid double-base propellant charges has been perfected, this being one of the causes of their use, despite energetic indices inferior to those of composite propellants. To increase the energetic properties of double-base propellants, aluminum powder and a solid oxidizer, for example ammonium perchlorate, are sometimes introduced into their composition. Such propellants are essentially "hybrids" of double-base and composite propellants [24, 55, 91, 111].

PROSPECTIVE HIGH-EFFICIENCY THRUST SOURCES

Prospective Oxidizers

Fluorine and some of its compounds (see Tables 8 and 9) are the most energetic oxidizers (Water, asbestos, sand burn in fluorine; water explodes with chlorine trifluoride and pentafluoride). During oxidation of fluorine, the combustibles evolve much more heat than during oxidation by oxygen (see Tables 2 and 3); metals form more volatile combustion products, but the amount of fluorine consumed by oxidation is 2.38 times greater than that of oxygen. The product of combustion of hydrogen in fluorine, HF, has good thermodynamic properties, but carbon with fluorine is less effective - the pentatomic molecules of CF_4 dissociate readily, removing part of the heat liberated during the combustion. All rocket fuels self-ignite with fluorine.

Below -188°C at atmospheric pressure, fluorine F_2 is a bright yellow liquid. It is kept in sealed tanks bathed in liquid nitrogen (at -196°C). It does not attack nickel, stainless steel, aluminum, or copper and its alloys, as it forms a protective film on their surface (the film is brittle and cracks at bending sites). Fluorine is extremely poisonous. Liquid oxygen difluoride OF_2 has a higher boiling point (-145°C), which facilitates its storage. It is even more toxic than fluorine. A prospective oxidizer is considered to be a mixture of liquid fluorine and liquid oxygen (the so-called flox, derived from the first two letters of fluorine and oxygen).

It is considered possible to increase the effectiveness of the oxygen oxidizer by adding to liquid oxygen up to 25% of liquid ozone O_3 (see Table 9), an allotropic modification of oxygen (this is the maximum quantity of ozone soluble in oxygen).

Pure ozone is extremely explosive and cannot be used. Ozone is more active than oxygen, i.e., fuels self-ignite on contact with it. On converting into oxygen O_2 , ozone evolves additional thermal energy. At the boiling point of liquid oxygen ($-183^\circ C$), the density of ozone is 1.57. Ozone is poisonous [86, 133, 135].

Maximum Indices of Bipropellants

The highest energy content (about 5700 kcal/kg) is that of the propellants lithium-fluorine and beryllium-oxygen (the same elements in the combination beryllium-fluorine and lithium-oxygen yield about 4800 kcal/kg). Any other combinations of the elements yield much less heat per kilogram of stoichiometric mixture (in particular, hydrogen-oxygen gives 2990 kcal/kg, and hydrogen-fluorine, 3090 kcal/kg). However, beryllium-oxygen and lithium-fluorine are inferior in terms of specific thrust to hydrogen with oxygen and fluorine, owing to condensation of the metal oxides in the course of expansion.

The best propellants from the standpoint of gas formation are hydrogen-oxygen (1234 nl/kg) and hydrogen-fluorine (1119 nl/kg); their gas formation increases sharply during incomplete combustion of hydrogen because of a very large specific volume, 11,120 nl/kg, which is 9-10 times as large as the volume of the products of its complete combustion. As a result, the maximum specific thrust of these propellants is obtained when approximately one-half of the hydrogen does not burn. The stability of diatomic HF to dissociation and its expansion adiabatic coefficient are greater than those of the triatomic H_2O , providing a higher engine thermal efficiency. Therefore, the specific thrust of the hydrogen-fluorine propellant is much higher than that of the hydrogen-oxygen propellant [55, 73, 128, 133].

Ternary Compositions

The highest values of theoretical specific thrust [kg sec/kg] correspond to tripropellants combining the maximum heat content of the beryllium-oxygen and lithium-fluorine combinations with maximum gas formation provided by hydrogen (the data are given for escape into a vacuum):

Hydrogen-oxygen	439	Hydrogen-fluorine	469
Beryllium-oxygen	328	Lithium-fluorine	456
Beryllium-hydrogen-oxygen	564	Lithium-hydrogen-fluorine ¹	520

Instead of lithium, lithium hydride LiH may also be taken (its calorific value is about 12,500 kcal/kg); the specific thrust in this case is slightly less, 509 kg sec/kg. The ratio of the components should be such that the metals burn completely, and hydrogen remains essentially free. It is assumed that beryllium can enter the combustion chamber of the engine in the form of a powder, and lithium, in the molten state (it melts at 180°C), while lithium hydride may be placed in the combustion chamber of a hybrid engine in the form of lumps (its melting point is 680°C) [117, 128, 133, 139, 140].

Boranes

Boranes (boron hydrides) are considered to be promising fuel components. They have a very high calorific value, over 15,000 kcal/kg. Diborane B₂H₆ is a cryogenic component with a moderately low boiling point, -92°C. Its calorific value upon formation of solid boric anhydride is about 17,000 kcal/kg, but its

¹According to other data, up to 600 kg sec/kg.

density is low, 0.43 at the boiling point. Pentaborane B_5H_9 (see Tables 1 and 3) is a light liquid; its calorific value upon formation of solid boric anhydride is 16,200 kcal/kg, and gaseous anhydride, 12,100 kcal/kg. Mixtures of pentaborane vapor with air are explosive and may self-ignite. Boranes are extremely poisonous (injure the central nervous system). Liquid hydrocarbon derivatives of boranes (for example, ethylpentaborane) are less poisonous. The heat of combustion of boranes is much higher upon condensation of the oxidation product of boron B_2O_3 (higher calorific value, see Table 2). This can be achieved only by expanding the gas in the nozzle, thus causing a decrease in thermal efficiency. In this connection, the effectiveness of boron hydrides, more than that of other fuels, depends on the specific operating conditions [73, 128, 133].

Free Radicals

An even greater specific thrust than the one developed by effective combinations of oxidizers and fuels can in principle be obtained from the chemical energy of free radicals, i.e., substances in a chemically unstable state, but the technical means of their utilization are still unclear. This is the limit above which the effectiveness of chemical propellants cannot be raised. Free radicals is the name given to particles possessing a free valence (atoms of hydrogen H, oxygen O, nitrogen N not combined into molecules; groups of atoms CH_3 , CH_2 , C_2H_5 , etc.). Dissociation (breakdown) of molecules into free radicals takes place with the absorption of energy from the outside; this energy is evolved upon association. Thus, dissociation of 1 kg of molecular hydrogen into atoms ($H_2 \rightarrow H + H$) requires 51,300 kcal/kg; when hydrogen atoms combine into molecules ($H + H \rightarrow H_2$), this energy is consumed in heating the gas (the process has long been applied in practice in atomic-hydrogen welding). In addition to evolving heat

upon association, hydrogen (and other fuel elements) may react with the oxidizer, so that the heat of association adds to the heat of combustion ($51,300 + 28,700 = 80,000$ kcal/kg, which is almost 2.8 times the ordinary heat of combustion of hydrogen).

Under ordinary conditions, free radicals can exist until their first collision with one another (a time of the order of millionths-thousandths of a second). In order to utilize free radicals as a propellant, they must be "preserved" in some fashion. Thus far, this has been accomplished only by deep cooling to temperatures close to absolute zero (for example, atomic hydrogen, oxygen and nitrogen at 4°K), when particle collisions practically cease. This requires complex and heavy cooling installations with liquid helium. At such temperatures, the atomic substance is a luminous solid. On heating to $30-40^{\circ}\text{K}$, active association takes place, accompanied by the evolution of a large quantity of heat and formation of a flame. A frozen "radical" substance is very dangerous in handling - random heating may cause a reaction in its entire mass and an explosion of tremendous power (for atomic hydrogen - similar to the explosion of an atomic bomb) [47, 73, 131].

Free Atoms in the Atmosphere

In the earth's atmosphere at a height of 80-100 km under the influence of ultraviolet rays of the sun, oxygen and nitrogen molecules dissociate into atoms. Their preservation in the free form is promoted by a very low pressure (0.01 Torr and less), when their collisions become rare. The heat of association of atomic oxygen ($\text{O} + \text{O} \rightarrow \text{O}_2$) is 3640 kcal/kg, and that of nitrogen ($\text{N} + \text{N} \rightarrow \text{N}_2$), 6050 kcal/kg. Catalysts may be used to force them to associate into molecules inside the engine of a flying vehicle which can be placed in an orbit 80-100 km high. The required compression in a ramjet diffuser may be reached at $M = 7$ to 10. If the fraction of

associated gas amounts to even 3-4% of the air passing through the engine, the evolution of heat per unit weight of air will already be approximately equal to that of modern turbojet engines. A vehicle operating on such a propellant will have an unlimited flight range [73].

Nature of Nuclear Fuel

A further increase of specific thrust may be obtained by using nuclear fuel as the source of thermal energy (up to $P_{sp} \approx 1000$ to 3000 kg/sec/kg), as a source of electrical energy (up to $P_{sp} \approx 50,000$ kg sec/kg) and finally, as a source of radiation, i.e., a photon flux ($P_{sp} \approx 3 \times 10^7$, i.e., 30 million kg sec/kg). Sources of a working substance must be used in addition to the nuclear fuel in this case.

In nuclear processes, one type of matter, a substance (i.e., matter possessing mass in a state of relative rest) is converted into another type of matter, electromagnetic radiation, whose particles, i.e., photons, move at the speed of light, 300,000 km/sec. When colliding with the particles of a substance, protons are absorbed and give up their energy, which is ultimately consumed in heating the substance. A complete transformation of 1 kg of the mass of a substance into energy, i.e., so-called annihilation, yields 21.5 billion kilocalories. It takes place in the interaction of antiparticles - electron and positron, proton and antiproton, neutron and antineutron, etc. Individual antiparticles can now be obtained with the aid of powerful electromagnetic accelerators, the largest of which have been built in the Soviet Union. However, to isolate and preserve "antimatter" appears impossible in the foreseeable future. A certain fraction of the mass of matter is converted into energy during the fission of heavy atomic nuclei and during fusion (combination) of light atomic nuclei. The former of these

processes, which forms the basis of the atomic bomb and atomic reactors, has now been generally mastered and, as we know, is practically applied in propulsion of stationary and ship engines. The second process, which occurs naturally in the sun and stars, has thus far been mastered only in the form of explosion (hydrogen bomb). Work being carried on in the USSR and abroad permits the hope that this process also will be harnessed.

The evolution of energy by the fission and fusion of atomic nuclei is determined by the difference in the packing energies of the elementary particles - protons and neutrons - in the atomic nuclei of different chemical elements. The total mass of protons and neutrons joined together in an atomic nucleus is smaller than the total mass of the same number of individually considered protons and neutrons. Their combination has consumed an energy equivalent to the defect (decrease) of their mass. For elements located in the middle of the periodic table, this energy is greater than for the lightest and heaviest elements. For this reason, combination of nuclei of light elements (deuterium, tritium, lithium) and fission of heavy nuclei (for example, uranium, plutonium) into parts which are the nuclei of elements of the middle of the periodic table proceed with the evolution of energy equal to the difference in packing energies [47, 55, 74].

Decaying Nuclear Fuel

The energy of currently mastered fission reactions of uranium-235, uranium-233 and plutonium-239 isotopes is approximately equal to 16 billion kcal/kg. The quantity of heat is given off by the combustion of 1500 tons of ordinary aviation petroleum fuel. In the active zone of a thermal nuclear engine reactor, the energy of the scattering fission fragments of atomic nuclei and electromagnetic radiation is absorbed and converted into thermal energy. It is transferred

to the working substance of the engine directly or via a heat carrier (for example, molten sodium or potassium or their alloy), which circulates between the active zone and the radiator heating the working substance [55, 74, 119].

Working Substance of Thermal and Electrothermal Nuclear Engines

Because of its high specific volume, the most advantageous working substance of a nuclear thermal rocket engine is of course hydrogen. In order to improve its heating by thermal radiation (which for all practical purposes is not absorbed by hydrogen up to 7000°K), carbon or metal additives decreasing the transparency may be introduced. Ammonia and water may also be used as working substances. It is postulated that when hydrogen is used, nuclear rocket engines with a solid active zone will have a specific thrust up to 750-900 kg sec/kg, those with a dust active zone, up to 1000-1100 kg sec/kg, those with a liquid active zone, up to 1500 kg sec/kg, and those with a gaseous zone, up to 2500-3000 kg sec/kg. Similar values of specific thrust can be obtained in the simplest electric rocket engines - electrothermal engines, involving transformation of nuclear energy into electrical energy, which is used in resistive heating elements or in an electric arc heater. The same hydrogen, ammonia, and water may be used as their working substance. For a small thrust of such engines, the reserve of working substance can be stored, not in condensed form, but in gaseous form at high pressure. In this case, a good working substance will be chemically inert helium, which is second only to hydrogen in specific volume. Its boiling point is close to absolute zero, around 4°K, which makes its storage in liquid form difficult [22, 55, 119].

Working Substance of Plasma Engines

At a temperature of several thousand degrees, the working substance converts into a plasma, i.e., a mixture of ion gas (charged positively) and electron gas (charged negatively). The presence of charges on particles of the working substance permits the use of an electric and magnetic field (instead of a gas-dynamical nozzle) for their acceleration. Electric rocket engines in which the acceleration of plasma particles is based on the electrodynamic principle are called plasma engines, and those based on the electrostatic principle, ion engines. In a plasma engine, expulsion of the working substance takes place as a result of passage of an electric current through the plasma, which is located in a magnetic field (the plasma is acted upon by the same forces as those acting on a conductor in the rotor of an electric motor). The initial working substance may be molten alkali metals (sodium, potassium, cesium) and other low-melting metals (indium, gallium), suspensions of powdered metals (for example, aluminum) on oil, metal hydrides (lithium hydride LiH , lithium aluminum hydride LiAlH_4), solid and liquid hydrocarbons, and gases - hydrogen, helium, nitrogen. The selection of a working substance is related to the manner of its conversion into a plasma and to the action on the engine material. The latter factor is very important, since plasma engines are usually designed for thrust from a few grams to a few hundreds of grams for a very long period of action (for many hours to several years of continuous operation). The first plasma engines were practically applied in a Soviet spacecraft, the Zond-2 automatic station of 1966. They operated in the attitude control system, maintaining the required position of the station relative to the sun [4, 22, 47, 126].

Working Substance of Ion Engines

In ion engines, free electrons are first detached from the plasma, and the positively charged ions carrying practically the entire mass of the working substance are accelerated in an electrostatic field. According to Coulomb's law, they stream toward the cathode, and on passing it, are neutralized by the returning electrons. The velocity of the reactive jet of an ion engine is of the order of tens to hundreds of kilometers per second; 1 kW of electric power can generate a thrust of about 3 g. Ion as well as plasma engines are recommended for use during long periods of continuous operation at a low thrust (grams) and with a correspondingly slight consumption of working substance.

The chief requirement on the working substance of ion engines is a low ionization energy. The best substance in this regard is cesium, a white, soft metal. Its density in the solid state is 1.903 g/cm^3 (at 20°C), it melts at 28.5°C , boils at 670°C , is extremely reactive - self-ignites in air, and vigorously decomposes water (with ignition of the hydrogen it displaces). The chemically less active cesium hydride CsH , whose density is twice as high and which contains 99.25% of cesium, can also be used. It decomposes at 400°C , and further heating makes it possible to obtain practically pure cesium vapor. Mercury, the only metal which is a liquid at ordinary temperatures, may also be used. The density of mercury is 13.56 g/cm^3 (at 20°C), it freezes at -38.9°C , boils at 357°C , and is appreciably volatile at ordinary temperatures. Chemically, mercury is almost as stable as silver. In contrast to cesium, mercury has a high ionization potential. In an ion engine, mercury vapor is ionized, not by detachment of its electrons, but by means of a special ionizer whose cathode emits a flux of electrons [22, 47, 126].

Thermonuclear Fuel

A more remote prospect is the use in flying vehicles of thermonuclear reactions taking place in the plasma at temperatures of millions of degrees, i.e., fusion of atomic nuclei of deuterium, tritium (heavy hydrogen with atomic weights of 2 and 3), lithium, and neutrons reacting with them. They yield considerably more energy than the fission of heavy nuclei - from 25 to 154×10^9 (154 billion) kcal/kg. It is possible to compress the plasma into a column and isolate it from the surrounding materials by means of magnetic fields, i.e. create a kind of "magnetic bottle" for the plasma, in which the thermonuclear reaction will take place. In practice, an inexhaustible energy source of thermonuclear engines will be natural water - each ton of water contains 16 g of deuterium. Thermonuclear conversion of the latter would provide 400-500 times more energy from each initial ton of water than the combustion of a ton of petroleum fuel [55].

Accumulation of Substance from the Outside

At a certain stage of technological development, it may be possible to use outboard sources of propellant and working substance. Thus, during the flight of an orbital vehicle in the upper layers of the atmosphere, accumulation of nitrogen and oxygen, their delivery into a liquefying unit, and separation in order to use liquid oxygen as the oxidizer in the chemical engine are possible. In outer space, accumulation and conversion of the extremely rarefied interstellar matter into propellant and working substance have been proposed [47, 124].

Part Two

LUBRICANTS AND TECHNICAL FLUIDS

CHAPTER 6

GENERAL DESCRIPTION OF LUBRICANTS

USES AND CLASSIFICATION OF LUBRICANTS

Basic Concepts

Lubricants for machines and mechanisms are substances artificially introduced between parts moving in relation to each other for the purpose of decreasing friction and its harmful consequences. The unproductive consumption of power consumed in overcoming friction is decreased tens and hundreds of times by lubrication. At modern velocities and loads, the friction components of engines and power transmissions would be destroyed in a few seconds without lubrication because of seizing, jamming, or melting and welding of the parts by the heat evolved during friction.

The antifriction action of lubricant may be based on two phenomena of different character. The first is the formation of an extremely fine protective film on the surface of contact between the solids, i.e., boundary lubrication. Friction involved in pure boundary lubrication remains external in nature, as in the absence of lubrication (its distinctive feature is a velocity discontinuity on the surface of contact). Such action of a lubricant is basic in rolling, gearing, and worm toothing, i.e., in forms of friction characteristic of rotor

bearings and reduction gears; in slipping, it is observed in the case of a high specific pressure or low velocity. The properties of a lubricant which provide for boundary lubrication are called lubricating capacity.

The second phenomenon on which the antifriction action of a lubricant may be based is the separation of solids at a sufficiently high velocity of their relative slip by a continuous layer of liquid, or hydrodynamic¹ lubrication (also called liquid lubrication). The character of friction thus changes radically, and external friction of solids is replaced by internal friction, i.e., by the viscosity of the liquid or gas (a distinctive feature of internal friction, is a smooth velocity change from layer to layer in the directional normal to the sliding surface). In pure hydrodynamic lubrication, friction wear of the parts is completely prevented. However, in the major friction components of modern gasturbine engines, this lubrication takes place only partially; it is used more extensively in piston engines. Usually, certain forms of combination of hydrodynamic and boundary lubrication are observed [12, 49, 59].

Types and Functions of Lubricants

Modern technology makes use of lubricants of different states of aggregation - liquid, solid and gaseous, as well as mixed (two-phase) lubricants. Liquid lubricants, i.e., lubricating oils, are predominantly used in engines and various mechanisms of flying vehicles. Solid (microlayered) and gaseous lubricants are considered promising for the high operating temperature of engine friction components; at the present time, they have limited applications.

¹Correspondingly, when a gaseous lubricant is used, this type of lubrication is called aerodynamic; there also exists the aerostatic principle of lubrication.

Two-phase (microinhomogeneous) lubricating greases consisting of a liquid oil and solid thickener are widely used in various units and parts of aviation and rocket technology. In addition to purely gaseous lubricants, two-phase lubricants with a gas base, i.e., aerosols (oil mist, smoke haze) also exist.

All types of lubricants fulfill two functions in machines and mechanisms: they reduce the force of friction between two parts in relative motion and protect their sliding surfaces from wear. In addition, liquid and gaseous lubricants fulfill a third function, also considered major, i.e., they remove the heat into which the work due to friction is converted. This function is no less important than the other two in the lubrication of high velocity friction parts. It is not fulfilled by solid (dry) lubricants and lubricating (plastic) grease, which are not fluid at the operating temperature.

In addition to their main functions, lubricants may fulfill other additional functions, i.e., protect parts from corrosion, seal the gaps between the parts (prevent the flow of gases through gaps) and carry the particles due to wear out of the friction components. In some cases, oil or a gaseous lubricant cools the engine parts heated by hot gases. Finally, oil can also be used as the working fluid in hydraulic installations.

Lubricants are usually understood to include not only antifriction lubricants, but also preservative and sealing lubricants, whose nature is similar. Some of the functions fulfilled by antifriction lubricants as additional functions are basic to these two categories and lubricants. Preservative lubricants are especially designed for protection of various equipment parts from corrosion and external contamination, and sealing lubricants are designed for sealing

threaded and other stationary joints, faucets, packing glands, technological seams, etc. [49, 59].

Classification

Figure 35 gives a model classification of aircraft lubricating materials according to their application (upper part of diagram) and composition (lower part of diagram). In first place are synthetic oils, since they are considered to be the most important in aviation technology in the immediate future. Traditional petroleum oils are in second place; essentially, control of their chemical composition and the additives employed change them into semisynthetic substances.

Lubricating greases based on petroleum oils and other natural products have contained synthetic thickeners and additives for a long time; they are chiefly used in friction components operating under not very severe conditions. For units and mechanisms subjected to strong heating or in contact with corrosive substances, synthetic greases and solid and gaseous lubricants are required. It is assumed that in the future, solid and gaseous lubricants may prove in engines of flying vehicles as well (in Fig. 35, the probability of utilization of various lubricants in the future is denoted by dashed lines) [59, 70, 71].

EXTERNAL FRICTION, BOUNDARY LUBRICATION, AND LUBRICATING CAPACITY

Nature of External Friction and Boundary Lubrication

The external friction of bodies (including machine parts and mechanisms) is the resistance to their movement relative to one another, arising on the surface

of their contact. Owing to irregularities of the microrelief of real bodies, the actual contact between them takes place only in certain areas constituting a minor fraction of the nominal surface of contact. In the presence of a compressive force, the actual pressure on such areas is very high, so that microscopic irregularities of one body are forced into the material of the other body. A great number of discrete (i.e., separate) friction bonds, so-called bridges, are formed between the bodies. Their formation and destruction during relative displacement (sliding) of the bodies is manifested in the form of the force of friction and frictional wear of the surface.

The force of friction acts in the plane of contact of the bodies in a direction opposite to that of motion. It depends on factors determining the strength and number of the friction bonds - on the conditions of contact (compressive force, temperature), microrelief of the surfaces (which in turn depends on their initial treatment and also on subsequent running-in and wear), on the mechanical properties of the surface layer of the materials (hardness, elasticity, limit shearing stress), on the physical properties (uncompensated electric field of the surfaces, diffusion, melting point), and on the chemical properties (oxidizability, possibility of formation of chemical bonds in the bridge).

As a first approximation, the force of external friction of solid bodies is proportional to the normal force P (Fig. 36) with which the body undergoing displacement is pressed to the surface of the counterbody (Amonton's law):

$$F = fP, \quad (6.1)$$

where f is the friction coefficient.

In the absence of lubrication in a medium of air, the minimum values of f ($f = 0.15 - 0.20$) are observed in the friction of steel, cast iron, and bronze surfaces and their combinations; for most other metals $f = 0.3 - 0.8$, and in the friction of copper over copper, $f = 1.3$. For unlike materials, f is usually lower than for like ones. The introduction of boundary lubrication, i.e., a thin film of lubricant in the presence of which solid contact is preserved, reduces the friction coefficient severalfold ($f = 0.01 - 0.1$).

Friction wear, which constitutes a gradual change in dimensions of the parts over their surface as a result of external friction,¹ is due to deformation or detachment of the material in the zone of individual microirregularities. The processes of microcutting, excavation, and plastic deformation (Fig. 36a), which take place even at small loads without lubrication, initially lead to an increase in roughness and the appearance of scratches, then develop from microphenomena into seizing and scoring over considerable portions of the surface. Ultimately, jamming or fracture of the mechanism takes place. Boundary lubrication at a moderate load prevents these dangerous phenomena. The boundary film adsorbed by the metal surface or chemically combined with it absorbs part of the deformation or is destroyed instead of the surface layer of the sliding parts. This promotes a reduction of metal deformation in the zone of each microbridge. If the deformation does not exceed the elastic limit, the opposing body flows around the microirregularities (Fig. 36b). Wear in this case is due chiefly to microirregularities which sharply project beyond the boundary of the main smooth portion of the lubricant film. It is usually slight, and during the initial period of

¹In addition to friction, wear may be caused by the mechanical action of sand, turnings and other solid particles that have entered between mating members (abrasive wear), by sharp pressure fluctuations or cavitation in the liquid (cavitation wear), and also by chemical agents, including those present in the lubricant (corrosive wear).

operation of a new or overhauled friction unit it promotes the running-in of its parts [12, 36, 49, 59].

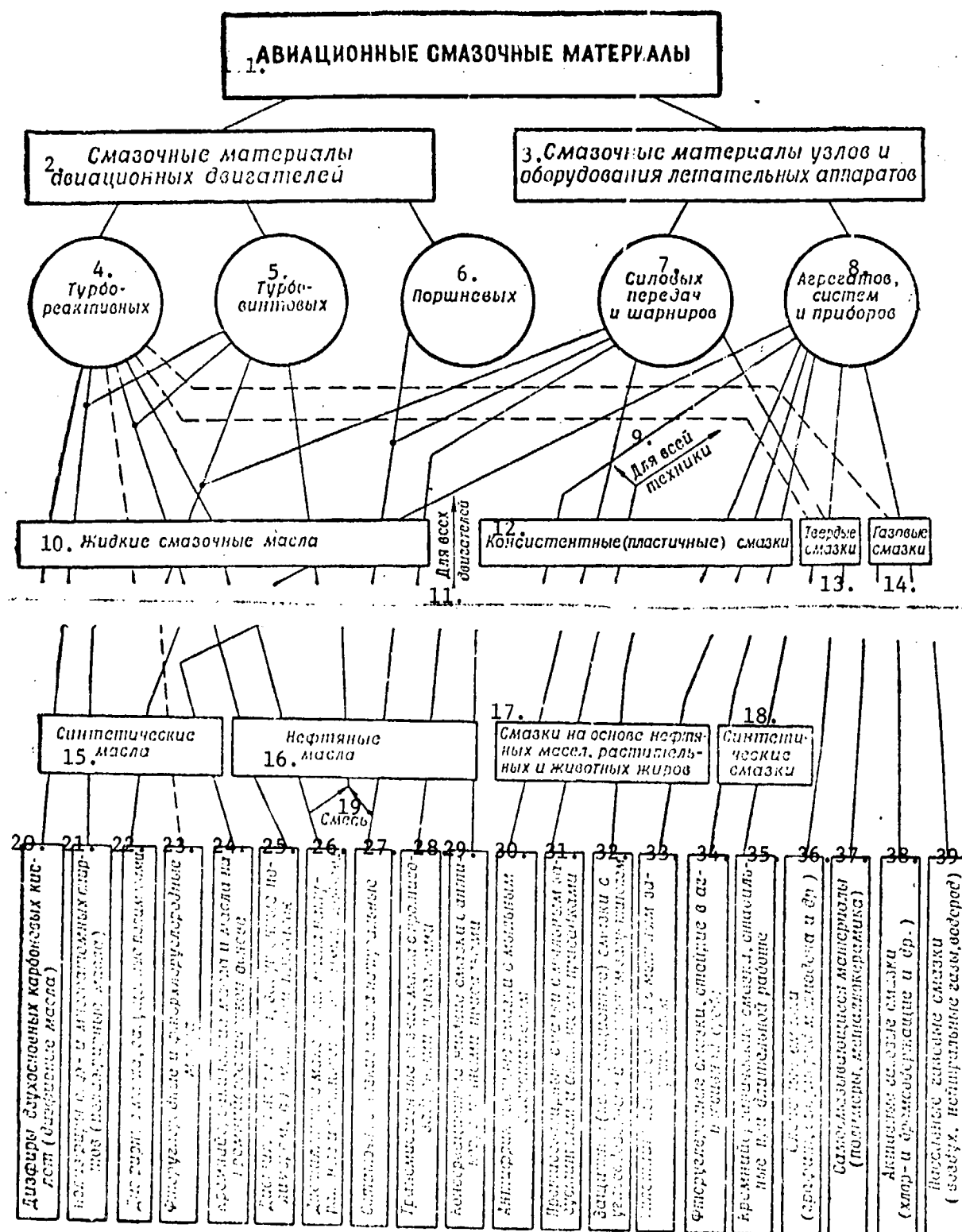


Рис. 35. Классификация авиационных смазочных материалов

Fig. 35. Classification of Aviation Lubricants.

Caption for Fig. 35.

Fig. 35. Classification of Aviation Lubricants. Key:

1. Aviation lubricants; 2. Lubricants for aviation engines; 3. Lubricants for components and equipment of flying vehicles; 4. Turbojet; 5. Turboprop; 6. Piston; 7. Power transmissions and bearings; 8. Assemblies, systems and instruments; 9. For all technical applications; 10. Liquid lubricants; 11. For all engines; 12. Greases (soft lubricants); 13. Solid lubricants; 14. Gaseous lubricants; 15. Synthetic oil; 16. Petroleum oils; 17. Lubricants based on petroleum oils and plant and animal fats; 18. Synthetic lubricants; 19. Mixture; 20. Diesters of dibasic carboxylic acids (diester oils); 21. Polyesters of di- and polyatomic alcohols (polyester oils); 22. Diester oils thickened with polymers; 23. Fluorocarbon and fluorochlorocarbon oils; 24. Organosilicon and organosilicon-base oils; 25. Distillate oils thickened by a polymer with a set of additives; 26. Distillate low viscosity oils, natural and with antioxidant additives; 27. Natural residual viscous oils; 28. Viscous transmission oils with antiseize additives; 29. Liquid conservation lubricants with anticorrosive additives; 30. Antifriction lubricants with soap thickener; 31. Antiseize lubricants with soap thickener and active additive; 32. Protective (preservative) lubricants with a hydrocarbon or soap thickener; 33. Sealing lubricants with a soap thickener; 34. Fluorocarbon lubricants resistant to corrosive media; 35. Organosilicon lubricants stable in prolonged operation; 36. Layered lubricants (graphite, molybdenum disulfide, etc.); 37. Self-lubricating materials (polymers, cermets); 38. Active gaseous lubricants (chlorine- and bromine-containing ones, etc.); 39. Passive gaseous lubricants (air, neutral gases, hydrogen).

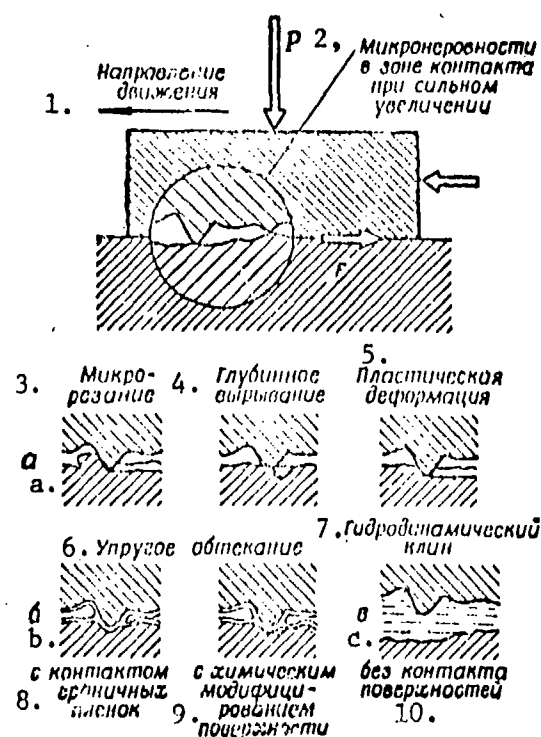


Fig. 36. Phenomena in the zone of a unit microirregularity during friction: Top - schematic diagram; a - external friction with destruction or residual deformation of surface in the absence of lubrication (or presence of inadequate lubrication); b - external friction with elastic contact in the presence of boundary lubrication; c - internal (liquid) friction in the lubricant layer. Key:

1. Direction of motion; 2. Microirregularities in the contact zone under high magnification; 3. Microcutting; 4. Excavation; 5. Plastic deformation; 6. Elastic flow; 7. Hydrodynamic wedge; 8. With contact of boundary films; 9. With chemical modification of surface; 10. Without contact of surfaces.

Rolling Friction

Boundary lubrication plays an essential role in ensuring a long service life of antifriction bearings - the chief type of friction component in modern aviation engines. The force pressing on a roller or roller in a race deforms it (Fig. 37). Resistance of rolling arises: the rolling body must deform the barrier forming in front of it. Periodic deformation causes fatigue wear, the appearance of microcracks, their merging, and point corrosion, the so-called pitting. The boundary oil film, which does not break down at high contact loads, decreases the fatigue wear; it is the first to be deformed, thus decreasing the contact stresses and deformation of the metal. The motion of rolling bodies also involves sliding relative to the dimple in the elastically deformed surface of the wheel; boundary lubrication reduces the friction coefficient of sliding between them. In certain antifriction bearings, the boundary character of lubrication is also observed in other areas of the sliding of balls and rollers in bearings - in the zone of contact with cages, with the ribs of bearing races, (in high-speed bearings, a hydrodynamic lubricant layer apparently forms in these areas).

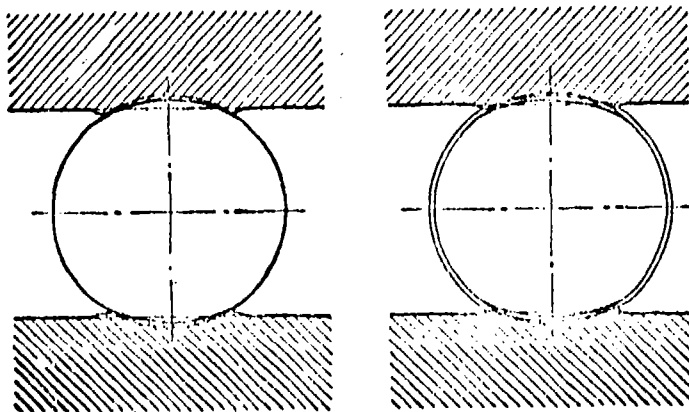


Fig. 37. Diagram of deformation of the race and ball (roller) in an antifriction bearing in the absence and presence of boundary lubrication.

The total friction coefficient for normal lubrication of aviation anti-friction bearings is of the order of 0.001-0.007 (this value is lower for ball bearings and higher for roller bearings) [11, 49, 57, 59].

Nature of Lubricating Capacity

The physicochemical basis of formation of the boundary film and hence, of lubricating capacity are the phenomena of adsorption and chemisorption.¹ Adsorption consists in an electric interaction of ions or electrically charged parts of liquid molecules with the electric field of metal atoms and ions forming the solid surface. For example, negatively charged particles of liquid molecules are attracted to positively charged ions of the metal surface (Fig. 38); onto the first row of polar molecules become superimposed the next rows. As a result, substances in whose molecules the electric charges are unevenly distributed (called surfactants) collect out of the oil on the surface of the metal. They include most synthetic oils, except polysiloxane ones.

The carriers of the lubricating capacity of petroleum oil are impurities of surface active substances present therein, i.e., organic acids, phenols, tars, and other organic compounds containing oxygen, sulfur, and nitrogen. They exhibit much stronger forces of adhesion to a metal surface than the hydrocarbon base of petroleum oil, whose molecules are nonpolar (the electric centers of gravity of their positive and negative charges practically coincide). If the oil contains an insufficient quantity of its own surface active substances, they can be added to it artificially; the corresponding oil additives are called antiwear additives. Thus, stearic acid (0.1%) used to be added as an antiwear additive to transformer oil for the purpose of lubricating turbojet engines.

¹Formed from the Latin words *chemie* - chemistry and *sorbere* - absorb, i.e., "chemical absorption" (of oil particles by a solid).

The adsorbed surface layer differs sharply in properties from the liquid from which it was formed. It does not contain the random thermal motion of molecules that is characteristic of a liquid; rather, it resembles a crystalline solid with an ordered arrangement of molecules, and may therefore be called quasicrystalline. The boundary friction inside such a layer may be compared to friction involved in the displacement of sheets in a stack of paper: likewise, the layers of molecules in the boundary oil film move relative to one another without breaking down.

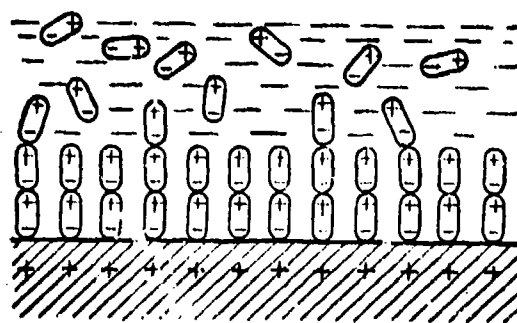


Fig. 38. Diagram of formation of a boundary film from polar molecules of a liquid on a solid surface.

Occasionally, between the boundary layer of a lubricant and the metal surface, chemical bonds are established, forming a thin surface layer of a new substance (sulfide, chloride, soap, etc.). This effect, called chemisorption, ensures an even stronger bond between the boundary lubricant and the metal surface. Essentially, it is a transition form to oxide and other surface films, which are no longer the lubricant itself, but a chemically modified layer of the basic material of the parts.

The thickness of the boundary layer of the lubricant is of the order of tenths of a micron. It may be represented as follows: if a smooth metal surface covered

with oil is wiped dry, the remaining film constitutes a boundary layer adhering to the metal. The small thickness of the lubricant boundary layer is explained by the fact that at a very small distance from the metal surface, the random thermal motion of the molecules already predominates over the forces of the surface tension. More viscous oils form a thicker boundary layer, since the thermal motion of the molecules has slowed down in these oils. Therefore, among oils of the same chemical nature, more viscous oils have a higher lubricating capacity.

A lubricant boundary layer is affected only under loads of short duration and not very high. Prolonged loads on the same areas or very large, even brief loads may cause such intense heating that the random thermal motion of the molecules overcomes the effect of surface forces and breaks up the ordered molecular layers [13, 18, 37, 59, 67].

Evaluation of Lubricating Capacity

The strength of a lubricant film as one of the characteristics of its lubricating capacity is estimated from the magnitude of the maximum load which the film is capable of withstanding before breaking. The test is usually carried out on a four-ball friction machine (Fig. 39), abbreviated FBM. The results of a series of one-minute tests conducted at different loads are used to plot the diagram of wear (Fig. 40). The breakdown of the film is manifested by a sharp increase in wear with increasing load, characterized by a salient point on the diagram of wear. The corresponding load of the start of seizing, or critical load (P_{cr}), is standardized by technical requirements placed on certain oils. The lubricating capacity is also determined on other friction machines, designed for tests of lubricants, from the decrease in the friction coefficient. It is different for different metals. [57, 59].

Severe Friction Conditions

Supercritical loads at which the boundary lubricant film breaks down may exist in reduction and worm power transmissions. The prevention of seizing under such conditions depends on the chemical processes in the surface layer of the metal. The condition of friction without seizing is a positive strength gradient, i.e., an increase in strength with depth into the material of the friction member. This condition is achieved if on the metal surface there is formed a film of oxides, sulfides, chlorides, and other compounds which has a lower resistance to shear and breaks down more easily on contact with the counterbody than the subjacent metal layers. Then the destruction processes do not affect the underlying layers, and wear affects only the chemically modified thin surface layer. Nevertheless, it is important that the destroyed films be instantaneously restored. This takes place if oxygen which has diffused through the lubricant layer or is dissolved in the oil has access to the rubbing surfaces [12, 18].

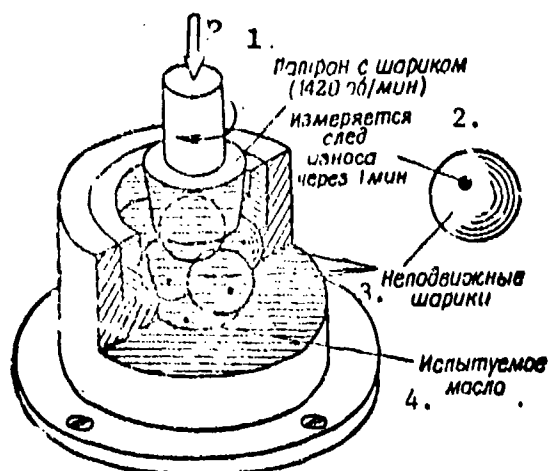


Fig. 39. Friction component of a four-ball machine for estimating lubricating capacity.
Key:

- 1. Chuck with ball (1420 rpm); 2. The mark of wear is measured in 1 min.; 3. Stationary balls; 4. Oil being tested.

Рис. 39. Угол трения четырехшариковой машины для оценки смазывающей способности

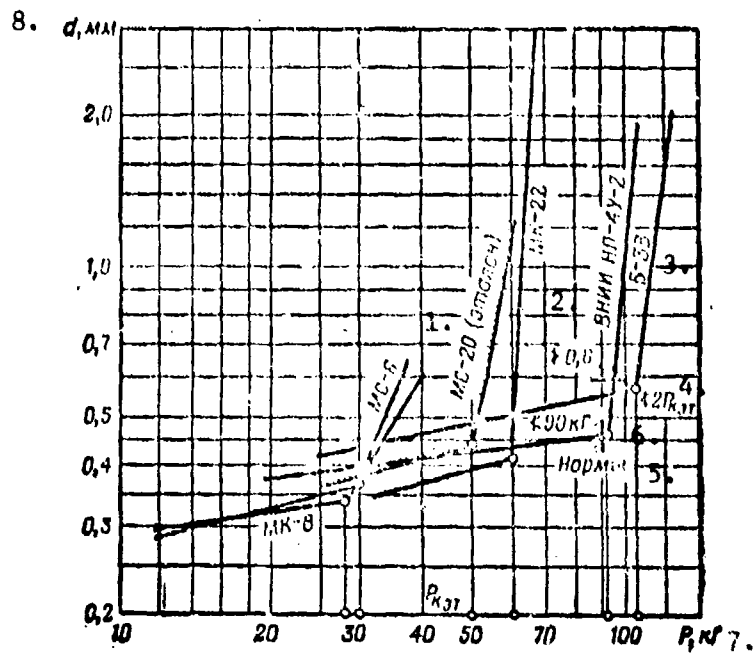


Fig. 40. Evaluation of the antiwear properties of oils on a four-ball machine: approximate dependence of the diameter of wear spot d on load P ; the elbow corresponds to the critical load of destruction of the oil film. Key:

1. (Standard); 2. VНИИ НП-4У-2; 3. Б-3В;
4. $\star 2P_{cr\ st}$; 5. Norms; 6. kg; 7. P , kg
8. d , mm.

Antiseize Properties

The protection from seizing by oxide films is insufficiently reliable. A positive role in this regard is played by an admixture of sulfur compounds naturally present in the oil; they ensure the formation of sulfide films. Most effective is the artificial introduction into the oil of phosphorus sulfur, and chlorine organic compounds, which decompose at high temperatures to form metal phosphides, sulfides, and chlorides. Such additives (tricresyl phosphate, mercaptobenzothiazole, "sovol", etc) are called antiseize compounds. The rate

of the chemical processes on a metal surface in the case of severe friction conditions is ensured by a sharp local heating of the microareas in contact. Thermal flashes associated with the destruction of friction microbridges reach several hundred or even one thousand degrees.

The substances formed on the friction surface usually have a lower melting point than the underlying metal layers, and during thermal flashes briefly pass to the liquid state. As a result, the shearing strength, work due to friction and heat evolution decrease; fusion of the metal itself and seizing and scuffing of the conjugated surfaces of the rubbing parts are prevented.

The antiseize qualities of a lubricant are particularly important under conditions where the friction surfaces are deprived of access of oxygen and of the possibility of naturally forming protective oxide films.

Wear, which is unavoidable under severe friction conditions, does not usually cause a decline in the quality of a surface; moreover, an accelerated running-in and smoothing out take place (particularly under the influence of phosphorus-containing additives) [12, 18, 59].

VISCOSITY (INTERNAL FRICTION) OF LUBRICANTS

Hydrodynamic Lubrication

In friction components with a hydrodynamic lubrication regime, the parts moving in relation to one another are not in contact (Fig. 36c), i.e., the friction takes place between layers of the liquid separating them. The internal friction

of a liquid is nothing other than its viscosity.¹

As follows from formula (1.16), in liquid friction with a constant transverse velocity gradient $\frac{dv}{dn} = \text{const}$, the friction force F per unit of sliding surface S is proportional to the dynamic viscosity of the lubricant μ , to the rate v of sliding of the rubbing bodies relative to each other, and is inversely proportional to the thickness h of the oil layer between the surfaces

$$\frac{F}{S} = \mu \frac{v}{h}. \quad (6.2)$$

This simplified formula was proposed by the author of the hydrodynamic theory of lubrication, Prof. N.P. Petrov (1883) for determining the force of friction in sliding bearings.

In a shaft-bearing couple, because of internal friction, the oil coating the shaft carries the neighboring oil layers into the wedge-shaped portion of the clearance. A pressure is generated which slightly raises the shaft. The rotating shaft "pumps" oil under itself and floats up on the oil stream it has generated. The higher the oil viscosity, the greater the load which the oil wedge can withstand. Similarly, during the reciprocating motion of a piston in a cylinder, the forces of internal friction pull the oil layers adjacent to the piston into the clearance. A pressure is produced which pushes the piston away from the cylinder wall; the transverse forces are transmitted from the piston to the cylinder wall through the oil layer without solid contact.

¹Concerning viscosity, units of its measurement and method of its determination, see pp. 48-49.

The maximum specific pressure $p_{sp} = P/S$ which a hydrodynamic lubricant layer can withstand is expressed by the semiempirical formula

$$p_{sp} = \mu v \phi \quad (6.3)$$

or

$$\mu \frac{n}{p_{sp}} = \phi' \quad (6.3)$$

where n is the number of revolutions per minute;

ϕ or ϕ' are functions of the geometry and operating conditions of the friction component, determined experimentally.

It follows from formula (6.3) that the supporting power of a hydrodynamic lubricant layer, as well as the force of liquid friction according to formula (6.2), increases with rising viscosity μ of the lubricant and sliding velocity v . Thus, from the standpoint of selection of oil viscosity, a contradiction arises. On the one hand, it is desirable to use an oil with the highest possible viscosity, since it increases the supporting power (allowable p_{sp}) and hence, the reliability of hydrodynamic lubrication, and prevents the oil from being squeezed out of the clearance. On the other hand, the higher the oil viscosity, the greater the force of friction and power loss consumed in overcoming the friction, so that it is desirable to use less viscous oils [36, 70].

Selection of Oil Viscosity

On the basis of the above, and considering the dependence of the viscosity of oils on temperature, for each engine or mechanism, an experimental selection is

made by taking the oil with the minimum viscosity at which liquid friction takes place under the highest temperature conditions of its operation (Fig. 41, right). As is evident from formula (6.3'), this viscosity should be higher the lower the velocity regime n and the higher the specific pressure. For a wide range of loads and rotational speeds, there exists an optimum value of the parameter $\mu n/p_{sp}$ to which correspond the lowest power losses due to friction. When μ or n decreases, just as when p_{sp} increases, the friction power grows owing to the formation of solid contact, and with increasing $\mu n/p_{sp}$ above the optimum value, the forces of internal friction increase and so does the power lost in overcoming them.

In a hydrodynamic lubrication regime and for a suitably chosen oil, the coefficient of sliding friction determined in accordance with formula (6.1) is tens and hundreds of times smaller than in the case of external friction without a lubricant ($f = 0.01 - 0.001$) [59, 70].

Effect of Pressure

At a high specific pressure, the oil viscosity increases exponentially:

$$\mu = \mu_0 e^{\alpha p_{sp}}, \quad (6.4)$$

where μ_0 is the viscosity at atmospheric pressure; coefficient $\alpha = 0.0023 - 0.0030$ for petroleum oils (higher α values correspond to more viscous oils).

The viscosity increase of petroleum oils becomes appreciable at $p_{sp} > 100$ atmospheres, which is entirely real for friction components of aviation engines and promotes the preservation of hydrodynamic lubrication as the load increases.

The viscosity of certain synthetic oils begins to increase only at a pressure greater than one thousand or several thousand atmospheres (for example, methyl and ethylpolysiloxanes). The rate of viscosity increase is slow at first, but as the pressure rises, the viscosity increases at an increasingly abrupt rate, up to the complete solidification of the oil. As the oil temperature rises, the effect of pressure on the viscosity decreases.

Viscosity of Oil for Antifriction Bearings

There exists a certain optimum oil viscosity, usually moderate, that provides for the longest service life of an antifriction bearing. At a lower viscosity, hydrodynamic lubrication of the cages and ribs of bearing races is not provided for, and boundary lubrication decreases as a result of a reduction in the thickness of the boundary film in the areas of solid contact. An excessively high viscosity increases the rolling resistance of balls and rollers, particularly when there is an abundant supply of oil, and intensifies the heating of bearings due to friction. At the same time, the cooling effect of the oil decreases. This may lead to tempering of the steel and a decrease of its hardness, and sometimes even cause recrystallization, a change in dimensions, and a distortion in the shape of the balls, rollers, and cages [59].

Regulations and Self-Regulation of Viscosity

The viscosity norms of oils are established at a temperature which more or less corresponds to the conditions of their use, most frequently at 100°C or 50°C; this temperature is denoted by a subscript on the letter designating viscosity. For reasons of practical convenience of measurement, not the dynamic viscosity (μ), but the kinematic viscosity $\nu = \frac{\mu}{\rho}$ is regulated. It is sometimes indicated in

the brands of oils, for example MK-8 is oil with viscosity $\nu_{50} \approx 8$ cS, and MK-22 is oil with viscosity $\nu_{100} \approx 22$ cS. In the case of lubricating greases, the dynamic viscosity (μ) is measured and regulated directly under the influence of a force, since they do not flow under their own weight.

However, friction components are not too sensitive to the viscosity of lubricants because of their self-regulation over a wide range of change of operational factors. When the viscosity is too high (for example, because of a low temperature of the oil), the work due to friction is also large. It is converted into heat, the lubricant heats up, and its viscosity decreases. The same effect is observed when the rotational speed increases. It is useful because it decreases the resistance at high speeds, when the hydrodynamic lubrication regime is ensured by a lower viscosity. The viscosity of a grease also decreases as a result of an increase in the deformation rate [59, 70].

VISCOSITY-TEMPERATURE AND STARTING CHARACTERISTICS OF LUBRICANTS

Importance and Methods of Representation

The viscosity of lubricants affects not only the lubrication regime, but also a number of operating characteristics - the required torsional moment on starting oil circulation in the lubrication system, cooling effect of the oil, its escape through seals, etc. The effect on some of these characteristics is manifested at low oil temperatures, and on others, at high temperatures. In this connection, of major practical importance are the control and correct allowance for oil viscosity over the entire temperature range existing under service conditions. Figure 41 shows a model diagram of the service requirements is determined by the slope of the viscosity-temperature characteristics.

The regulation and control of the slope of the viscosity-temperature characteristic of oils are carried out in different ways (Fig. 42):

a) by limiting the viscosity at a high temperature and at the upper end at a low temperature (for example, for diester oil ν_{100} no less than 3.2 cS, ν_{-40} no higher than 2000 cS);

b) by means of the magnitude of the viscosity ratio at different temperatures (for example, for MK-6 oil, the ratio ν_{-20}/ν_{50} no greater than 4.65; for MS-20 oil, the ratio ν_{50}/ν_{100} no greater than 7.85);

c) by means of the temperature coefficient of viscosity in the temperature range from $t_a = 0^\circ\text{C}$ or 20°C to $t_b = 100^\circ\text{C}$, which is determined by the formula
$$\text{TCV} = 100 \frac{\nu_a - \nu_b}{(t_a - t_b) \nu_{50}}$$
 for example, for MK-22 oil, $\text{TCV}_{20-100} = \frac{\nu_{20} - \nu_{100}}{\nu_{50}} \times 1.25$ no greater than 11);

d) by means of the viscosity index (VI), which represents the slope of the viscosity-temperature curve by comparison with curves of standard oils (dashed lines in Fig. 42), and is determined in practice by means of tables of values of ν_{50} and ν_{100} ; the milder the slope of the curve, the higher the viscosity index (for example, for MS-20S oil, the VI norm is no less than 85 [36, 65, 70]).

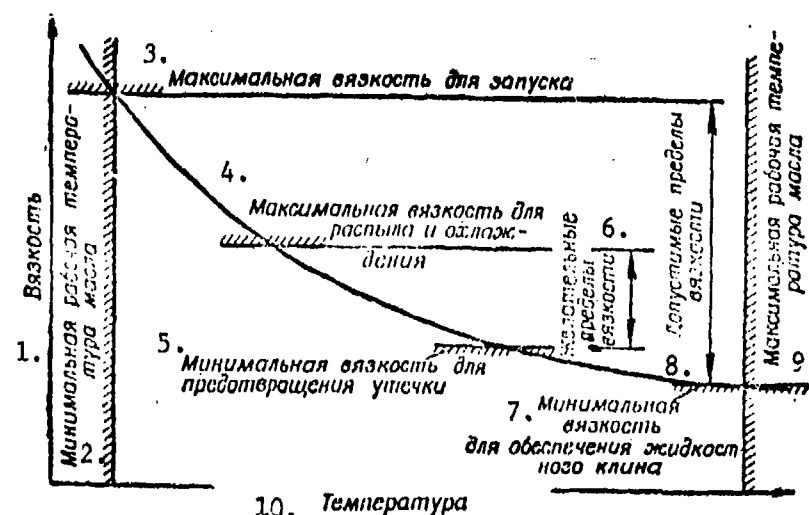


Fig. 41. Requirements placed on the viscosity-temperature properties of oils. Key:

1. Viscosity; 2. Minimum working temperature of oil;
3. Maximum viscosity for starting; 4. Maximum viscosity for spraying and cooling;
5. Minimum viscosity for preventing leaks; 6. Desirable viscosity limits; 7. Minimum viscosity for the formation of liquid wedge;
8. Allowable viscosity limits; 9. Maximum working temperature of oil; 10. Temperature

Starting Properties

The minimum oil temperature up to which engine starting is possible is determined by two factors related to increasing oil viscosity with decreasing temperature: the increase in the resistance of the rotation of the engine by the starter and the decrease or interruption of the supply of oil to the friction components.

The main portion of the moment of resistance to rotation when the engine is started on cold oil is due to the work of compression of air; the fraction of friction in the bearings and drive of oil units is 3-5%. However, when the temperature is lowered, it becomes commensurate with the loss due to air compression.

As a result, the duration of the starting increases and its reliability decreases, or the starting becomes altogether impossible if the power of the starter is not adequate to overcome the increased resistance of the rotor. The maximum oil viscosity up to which the starter can start the engine is usually considered to be 2000-5000cS, depending on the engine type; a more accurate value of this viscosity depends on the design of the engine and power of the starter. The temperature corresponding to this viscosity may be found for each oil from its viscosity-temperature characteristic (for example, from the curves shown in Fig. 47).

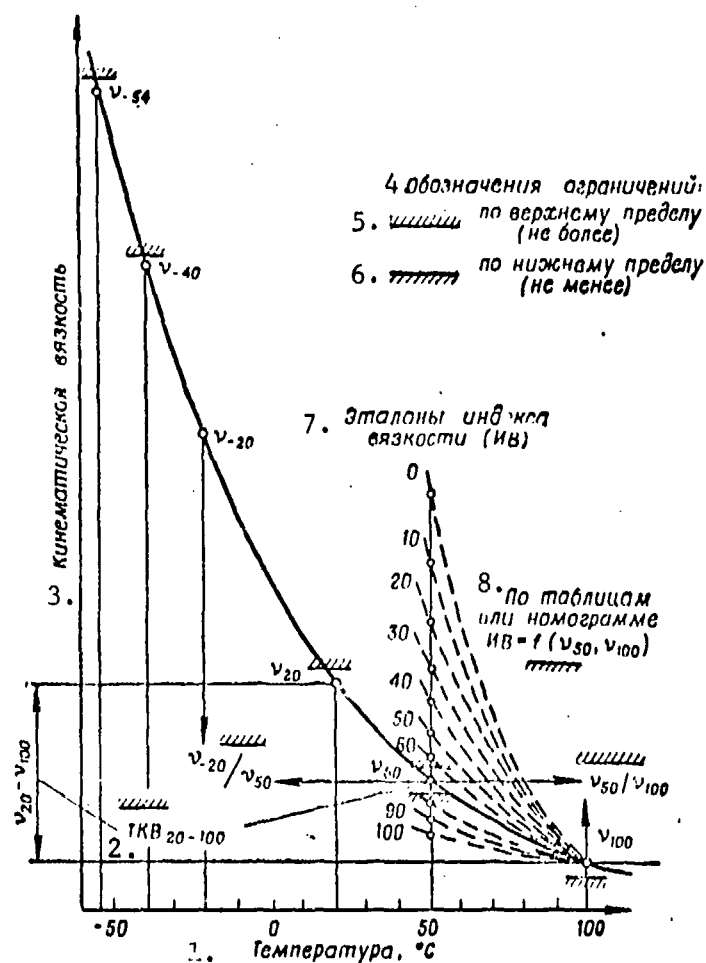


Fig. 42. Ways of estimating and limiting the viscosity-temperature characteristic of oils; temperature coefficient of viscosity in the range from 20 to 100°C,

$$TCV_{20-100} = 1.25 \frac{v_{20} - v_{100}}{v_{50}}.$$

Caption for Fig. 42

1. Temperature, °C; 2. TCV₂₀₋₁₀₀; 3. Kinematic viscosity; 4. Symbol of limitations; 5. At upper limit (no greater than); 6. At lower limit (no less than); 7. Standards of viscosity index (VI); 8. From tables or monogram VI

$$\nu = f(\gamma_{50}, \gamma_{100}).$$

Discontinuation of oil circulation in the system takes place at a viscosity of the order of 20,000 cS. However, an appreciable decrease in oil supply to the major friction components of aviation engines, as well as a considerable worsening of spraying and distribution of oil within the friction components usually take place when the viscosity attains about 5000 cS, not much greater than the limiting viscosity of start-up of the rotor. For this reason, a significant increase in starter power cannot be regarded as a means of overcoming poor starting properties of an oil, since this may result in the breakdown of the friction components. In engines whose rotor is connected to the turbostarter by a hydraulic clutch, at a viscosity of several thousand centistokes, the filling of the hydraulic clutch with oil worsens, causing a sluggish acceleration of the rotor [1, 37, 59, 70].

Special Properties Under Intermediate Operating Conditions

There is an intermediate oil viscosity and corresponding oil temperature during starting at which the motion of the oil causes a decrease in its viscosity; this makes it easier for the engine to achieve full operation after the start of rotation. This is explained by structural changes in the oil as its temperature changes. As the temperature goes down, the disordered thermal motion of liquid molecules which continuously breaks the intermolecular bonds slows down. The bonds become stabilized, and increasingly stronger molecular associations are

formed. The enlargement of the elements of internal structure of the liquid is manifested in an increase of its viscosity. However, the motion of such a liquid breaks down the associations, and its viscosity decreases. Thus, at low temperatures, oil viscosity depends on the transverse velocity gradient $\frac{dv}{dn}$ (sometimes called the viscosity anomaly).¹ This relationship is manifested even more markedly in the case of formation in the oil of microparticles of solid phase from paraffin hydrocarbons crystallizing at low temperature. When the oil is in the stationary state, the paraffin crystals form a loose framework that breaks down when acted on by an external force (acceleration by starter, pressure due to pump) [36].

Means of Improving the Starting Properties

The following rule holds for oils of the same chemical nature: the lower the viscosity, the less it increases as the temperature is lowered, i.e., the better the starting properties of the oil. However, decreasing the viscosity of oils as a means of improving the viscosity-temperature characteristic is usually inadmissible because of the necessity of having a sufficient viscosity at the maximum operating temperature. Good viscosity-temperature properties characterize synthetic oils (with the exception of fluorocarbon oils).

An important means of obtaining sufficiently viscous oils operating satisfactorily at low temperatures is the thickening of low-viscosity petroleum or synthetic oils by a high-molecular polymer (for example, polymethacrylate, polyisobutylene). This method can be used to increase the oil viscosity at the basic operating temperature to the required value while preserving the slope of the viscosity-temperature characteristic typical of a low viscosity oil.

¹This type of properties of viscous liquids are called structural-mechanical properties. They are particularly characteristic of greases and are discussed in more detail in Ch. 10.

Large, heavy polymer molecules, which are hundreds and thousands of times larger than the molecules of the liquid base, inhibit its flow and increase the internal friction between the oil layers, raising the viscosity level. At the same time, the temperature dependence of viscosity remains approximately the same as for the low-viscosity base (Fig. 43), so that the degree of decrease in the cross section of the flow of the low-viscosity liquid due to the large polymer molecules remains practically unchanged at any temperature. The chief disadvantage of thickened oils is a gradual mechanical degradation ("grinding") of the thickener during friction, and also its thermal degradation at high temperature. The degradation of additives depends considerably on their chemical nature and molecular weight. Therefore, of major importance is the choice of thickener, which must be sufficiently stable under the conditions of use of the oil [42, 87].

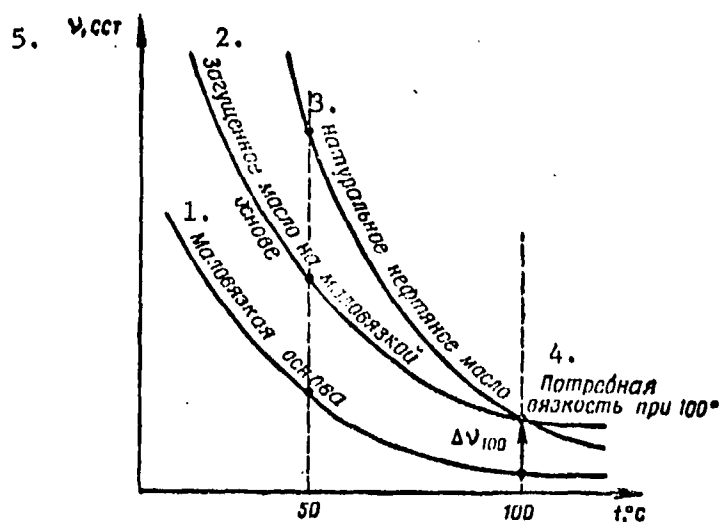


Fig. 43. Viscosity-temperature characteristic of natural and thickened oils (schematic diagram)
Key:

1. Low-viscosity base; 2. Thickened oil with low-viscosity base; 3. Natural petroleum oil; 4. Required viscosity at 100°C; 5. ν , cS

Solidification of Oils

Oils do not have a distinct temperature of transition from the liquid to the solid state. The transition boundary is conventionally considered to be the solidification temperature at which loss of oil mobility takes place. Solidification may be due to two different processes: a gradual increase in viscosity up to conversion of oil into an amorphous vitreous mass with a disordered arrangement of the molecules (without any indications of crystalline structure), or the formation of a crystalline framework of high-melting paraffin hydrocarbons.

In the production of oils, efforts are made to remove high-melting paraffins in order to ensure a low solidification temperature of the oils. Special additives, i.e., depressors, which prevent the growth and intergrowth of paraffin crystals, are introduced into certain grades of oil. A depressor can lower the solidification temperature of oils by 20-30°. In the absence of paraffin hydrocarbons, or when they are present in slight quantities, a depressor cannot block the solidification of an oil caused by an increase in viscosity. In this case, the solidification temperature of the oil can be lowered only by diluting it with fuel.

It should be kept in mind that the lower temperature limit of starting of a cold engine is related to the viscosity-temperature characteristic of the oil; it is usually much higher than the solidification temperature. At the solidification temperature and a lower temperature, draining of the oil is practically impossible [36, 59, 70].

PHYSICAL STABILITY AND HOMOGENEITY OF LUBRICANTS

Vaporizability

The vaporization of oils and lubricant greases under service conditions causes irreversible changes in their composition and properties. The simplest indication of the presence of readily vaporizing fractions in the oil is the flash point. It is determined in an open crucible or in a special instrument with a closed crucible which limits the dispersal of vapor (it is lower than in an open crucible).

A more complete evaluation of the vaporizability of oils is given by fractional distillation, but it cannot be carried out in the same manner as for fuels: the boiling temperature of oil fractions at atmospheric pressure is higher than the temperature of thermal decomposition of certain substances entering into the composition of the oils. Therefore, the fractional composition of oils is determined in a vacuum apparatus at a pressure of 3-4 Torr, which provides for the necessary lowering of the boiling temperature. Another method is based on vaporization of the oil at atmospheric pressure from a thin layer in flat-bottom aluminum cups (for each 20°C rise in temperature, one cup is removed and weighed). Thus, one can determine the difference in the fractional composition of oils without considering the actual boiling temperature of their fractions (see Fig. 48) [37, 59].

Preservation of Physical Properties

The narrower the fractional composition of an oil, the less its properties change as a result of vaporization, and the more physically stable the oil. The

limit corresponds to the oil which boils at a constant temperature, and whose properties undergo no change on vaporization. In oils of a wide fractional composition, after the evaporation of light fractions, the fraction of heavy, viscous components increases. This is readily manifested in more difficult cold engine starting.

The vaporizability of lubricant greases is estimated from their weight loss at standard conditions. It causes a considerable change in their performance characteristics [37].

Mechanical Impurities and Water

The physical inhomogeneity of oils as well as fuels is determined by the absence of mechanical impurities and water droplets. Mechanical impurities present in the oil are observed with the unaided eye by inspecting a drop deposited on convex glass; if necessary, the oil film is inspected through a magnifying glass or under a microscope. A qualitative check of the absence of water in the oil is made by heating the oil to 150°C in a test tube. Liquid water changing into vapor manifests its presence in the foaming of the oil and a characteristic crackling noise. The absence of liquid water in lubricant greases, which melt in the course of the determination, is established in similar fashion.

The appearance of a suspended mass of fine mechanical impurities or water emulsion in the oil increases the oil viscosity. However, the main damage done by physical inhomogeneity consists in breaking up the continuity of boundary lubrication, in the abrasive and corrosive action of the inclusions, and also in their initiating influence on sedimentation [59, 64].

THERMAL OXIDATIVE AND THERMAL STABILITY OF LUBRICANTS

High-Temperature Chemical Changes

During heating caused by the influx of heat and friction, chemical processes oxidation and decomposition - take place in oils and lubricant greases. They result in the formation of solid and pasty deposits contaminating the engine or the lubricating mechanism, in an increase of the oil viscosity, and in an intensification of corrosive activity. Oxidation takes place mainly at temperatures up to 300°C under conditions of contact with atmospheric oxygen or other oxidizing agents and with catalytic reactive metals, mainly with copper and copper alloys. The stability of a lubricant to oxidation at high temperatures is called thermal-oxidative stability. At higher temperatures (300-400°C and above), processes of decomposition of molecules, detachment of hydrogen, etc. predominate. The stability of a lubricant to decomposition at high temperatures is called thermal stability [37, 58, 70].

Oxidation in the Volume

Extensive oxidation of an oil proceeds both in the volume and in a thin layer on hot parts; oil mist in the cavities of the engine undergoes a limited oxidation (although apparently essential for further processes). In the volume, oxidation takes place inside the oil tank, oil pans and lines in the presence of air (dissolved, bubbling, or foam). Oxidation forms high-molecular organic acids and alcohols, phenols, resins and solid products of their condensation, poorly soluble in oil. They separate in the form of a dark powdered sediment or particles 1-2 mm in size which clog filters, nozzles, and oil injectors. Coarse resin fragments resembling colophony in external appearance are occasionally formed in

the oil tank. Intensive sedimentation in petroleum oils begins at 120°C, and in synthetic oils at a higher temperature. The thermal-oxidative stability of an oil is estimated during its analysis from the amount (in %) of sediment and from the acid number after oxidation, and in some cases from the increase in oil viscosity after testing at 120°C or 175°C in the course of 10-14 hr, air or oxygen being blown through in contact with copper and steel [37, 58, 64].

A different character is that of sedimentation in the oil system of piston engines, where condensation of moisture from fuel combustion products is possible. Oxidation products, dust particles and products of metal wear collect on the surface of fine water droplets. A rough, greasy mass, about half of which consists of water, precipitates out. The process of formation of such a sediment is more rapid the lower the temperature conditions of the engine and the more favorable the conditions for water condensation.

Oxidation in a Thin Layer

Light oil fractions vaporize on hot surfaces of bearings, pistons, and other parts. The remaining heavy fractions are first converted into resinous ones, then into hard lacquer or abrasive deposits consisting mainly of carbon. Lacquer formation proceeds continuously, and its rate increases with rising temperature. Lacquer changes the working clearances in the friction components, affects heat exchange, and causes seizing of piston and packing rings [58, 59, 70, 71].

In analyzing oils, the thermal oxidative stability in a thin layer is evaluated in different ways: from lacquer formation in the film flowing down an inclined hot plate; on the hot piston surface in a device simulating an engine

without fuel supply); in aluminum cups in a special heater (lacquer forming unit), etc. [64]. Of particular interest is testing on a unit with a high-speed anti-friction bearing which produces a scheme of contact of oil with oxygen and metal surface that is natural for an engine, and also thermal flashes and electrical phenomena initiating oxidation [66].

Influence of Oil Composition on Oxidation

The composition of aviation petroleum oils include mainly cyclic hydrocarbons whose molecules contain different numbers of aromatic or naphthenic rings and paraffin side chains. Most stable to oxidation are slightly branched aromatic hydrocarbons with no side chains. They also protect the remainder of the oil from oxidation. This is due to the fact that their oxidation forms phenolic compounds which serve as antioxidants and break off the chains of oxidative reactions. In this connection, excessive oil purification in which useful aromatic hydrocarbons are removed decreases the stability of the oil. An even greater antioxidant effect is that of phenolic additives such as ionol artificially introduced into oils.

As a rule, synthetic oils are marked by a higher thermal oxidative stability than petroleum oils. This accounts for the extensive use of synthetic oils in aviation [40, 106].

Thermal Stability

In stability to decomposition at high temperatures, petroleum oils for turbojet engines (if they are protected from oxidation) are not inferior to synthetic oils, with the exception of fluorocarbon oils. However, at 400°C and

above, all modern lubricants of organic origin decompose, with petroleum oils converting into a scalelike carbonaceous mass. Certain synthetic oils prepared from esters have the advantage that their decomposition products are volatile or completely soluble in oil, i.e., are safe for use in engines.

A temperature of the order of 400°C acts on the oil of piston engines which has reached the bottom of a piston. On losing its volatile substances, the oil carbonizes and forms a deposit. On contact with oxygen, the deposit gradually burns up; its layer is thinner, the higher the temperature conditions of the engine. For this reason, the quality and consumption of oil during prolonged operation of the engine have practically no effect on the thickness of the deposit. However, the rate of formation of the deposit before its stabilization depends on the thermal stability of the oil.

The thermal stability of certain oils is controlled by means of the coking capacity, i.e., the carbon residue (in %) after the evaporation and calcination of an oil in an instrument with limited access of air. However, comparison of oils of different compositions according to this index does not correspond to their behavior in the engine [59, 66, 70, 106].

Stabilization of Indices

During the operation of an oil in an engine, the indices of thermal oxidative stability and thermal stability change. A sharp decline of all the indices takes place in the first few hours of engine operation on fresh oil (Fig. 44). However, these changes subsequently take place less abruptly as a result of the oil working in the engine. Stabilization promotes filtration of the oil,

its centrifuging inside the engine shafts, formation of phenolic antioxidants, etc. As is evident from Fig. 44, certain indices are practically completely stabilized [8].

Radiation Resistance

One of the forms in which oil stability is manifested, closely related to resistance of oxidation and decomposition, is their stability to nuclear and cosmic radiation.

The action of radiation fluxes of both quantum type (gamma radiation) and corpuscular type (α particles, protons, neutrons, etc) is chiefly energetic in character. Their absorption is associated with a partial rupture of the bonds between the atoms in hydrocarbon molecules or detachment of electrons from them. This results in the formation of a multiplicity of free radicals and ions which initiate chain processes of oxidation and polymerization. These processes lead to an increase in the viscosity (at a very high dose, to gelatinization) and acid number of oils. Detachment of part of the hydrogen atoms leads to the formation of high-carbon condensation products, and the oil darkens. Thickened oils are first diluted as a result of destruction of the polymer chains of the thickener, then thicken like other oils.

Oils characterized by a high degree of stability to high temperature oxidation and decomposition simultaneously differ in a high radiation resistance. A considerable change in the properties of aviation synthetic and petroleum oils takes place at a total absorbed radiation dose of more than 2×10^8 rad. Special synthetic oils and lubricants have a higher radiation resistance. Anti-oxidant additives practically do not increase the radiation resistance: as a

result of interaction with a large quantity of active products, they wear out rapidly [32, 70].

CORROSIVE ACTIVITY OF LUBRICANTS

Content and Action of Organic Acids

The chief components of synthetic oils and the hydrocarbons forming the base of petroleum oils do not react with metals. Organic acids usually present in oils and lubricant greases as impurities are corrosive toward metals. They enter the oils from the raw material; they are partly formed in the course of use and in some cases during storage: in petroleum oils - as a result of oxidation of hydrocarbons, and in synthetic oils - during hydrolysis of esters (their decomposition with the participation of water). In lubricant greases, organic acid may also form as a result of hydrolysis of the soap thickener.

The content of organic acids in oils and lubricants is estimated as in fuels, from the amount of alkali - potassium hydroxide KOH - necessary for their neutralization. The index of their content in 1 g of lubricant is called the acid number. For fresh petroleum oils, it is small, no greater than 0.04 - 0.1 mg of KOH/g (depending on the grade of oil), but increases many times during the operation of an engine (Fig. 44a). The acid number of fresh synthetic oils is higher; for diester oils, up to 0.22-0.25, and polyester oils, from 4.5 to 6.0 mg of KOH/g. However, during the operation of engines, there is no sharp increase in the acid number of these oils, and in some of them it even decreases. The increase in the acid number of diester synthetic oils takes place upon their moistening (they are more hygroscopic than petroleum oils). In this connection, steps must be taken to protect them from penetration of atmospheric moisture.

As a whole, the corrosiveness of synthetic oils is higher than that of petroleum oils. For this reason, a special selection of metals and coatings stable in these oils is required.

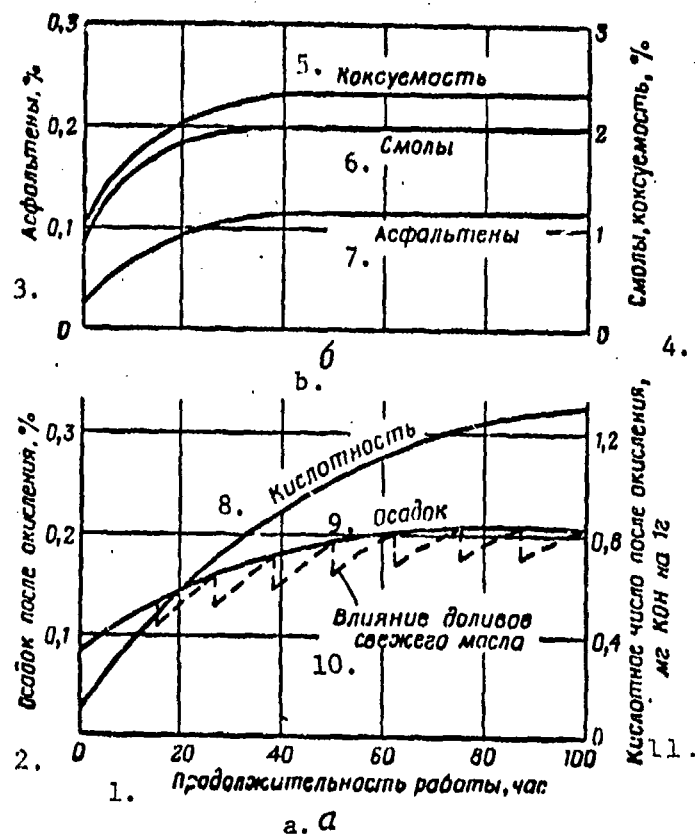


Fig. 44. Change in certain indices of thermal oxidative stability of oils during engine operation (according to the state before successive additions): a - in a turbojet engine; b - in a piston engine. Key:

1. Duration of operation, hr; 2. Sediment after oxidation, %; 3. Asphaltene, %; 4. Resins, coking capacity, %; 5. Coking capacity; 6. Resins; 7. Asphaltene; 8. Acidity; 9. Sediment; 10. Effect of fresh oil additions; 11. Acid number after oxidation, mg of KOH per g.

The corrosive action of organic acids is manifested in friction components only at elevated temperatures (above 50°C), particularly on heating in the friction zone. A characteristic corrosive-frictional point wear is observed in the case

of oils with a high acid number. It is possible that the pitting wear of anti-friction bearings is due to a combined corrosive and mechanical action on the surface of the metal. Contact with the metal in turn promotes an increase in the acidity of the oil. However, there is no dependence between the acidity of fresh oil and the corrosion it causes during operation, since different acids have different activities. Therefore, the corrosiveness of an oil is estimated from the change in the weight of metallic plates under conditions simulating the conditions of use to a given extent, and the acid number of fresh oil is determined in order to check the technology of its production [37, 59].

Additives

In order to decrease the activity of certain synthetic oils in relation to metals, anticorrosive additives are used, in particular, mercaptobenzothiazole (an organic nitrogen-containing sulfur compound), which is also used as an anti-seize additive. The action of this and most other anticorrosive additives is determined by their own corrosive activity, i.e., the ability to form a protective film on the metal surface (it should be kept in mind that their active influence on certain coatings may prove harmful). The anticorrosive action of additives is usually combined with antioxidant action, since the protective film insulates the oil from direct contact with nonferrous metals, which catalyze oxidation of the oil. Another method of preventing metal corrosion is to neutralize the acid compounds with a slight excess of alkali if the latter is safe for a given metal. This method is used to improve the protective properties of lubricant greases and certain grades of oils used in ground equipment [37, 59].

Action of Sulfur

Sulfur compounds present in oils for engines are not active at ordinary working temperatures and do not cause corrosion. They manifest themselves only under severe friction conditions, when the corrosive action of the oil plays a positive role (prevents seizing and welding). In certain heavily loaded reduction and worm mechanisms, corrosive oils are deliberately used, since the danger of corrosive wear of such mechanisms is less than the danger of seizure. Oils for these mechanisms contain a high concentration of organic acids and sulfur compounds (certain oils even contain free sulfur) [67, 70].

Effect of Oil on Rubber and Packing Materials

The industrial-rubber and other nonmetallic parts used in lubricating systems are made of special materials which are stable in contact with the oil grades designed for them. Nonoil-resistant grades of rubber, paronite and other non-metallic materials are destroyed by the chemical and physical (dissolving) activity, not of the impurities, but of the oil base itself, which attacks these materials. They gradually swell or shrink, their strength decreases, they lose their elasticity, and brittleness and cracks appear. The oil thus becomes contaminated with products of reaction with rubber, and with particles of corroded seals. The intensity of the action of oils on rubber increases with rising temperature. In the composition of petroleum oils, aromatic hydrocarbons are most corrosive to rubber and paronite, followed by naphthenes; paraffin hydrocarbons are the most passive. In this connection, for a series of aviation oils, a norm has been established for the lower limit of the aniline point (temperature of demixing of oil with aniline: the higher this temperature, the smaller the quantity of aromatic hydrocarbons present in the oil). Rubber brands 4410, 9831

and others used in aviation engines are practically stable when standard petroleum oils are employed. As a rule, synthetic oils are marked by a more corrosive action toward rubber and require the use of special rubber compositions stable toward them. In particular, rubber of brand 3825 is not attacked under conditions of contact with diester oil [37].

GENERAL REQUIREMENTS PLACED ON LUBRICANTS

Factors Dependent on the Lubricant

The quality of a lubricant has a certain influence on the working capacity of engines and other lubricated mechanisms and components of flying vehicles. Primarily, it determines their reliability in the course of a specified service period, and also the ease of starting of the engine and speed with which it reaches normal operation (or the resistance to shear in other devices). Under any service conditions, the lubricant should form a reliable interlayer between the rubbing surfaces which will decrease the friction and wear. In friction components whose construction and operating conditions are designed for hydrodynamic lubrication, the lubricant should provide for the formation of a continuous liquid layer and not leak out too fast or be thrown out of the clearances. At the same time, it must not give rise to large forces of intraliquid friction, which require a significant power consumption. In components with boundary lubrication (portions of contact during rolling and gearing) and also during brief breakdowns of hydrodynamic lubrication, the lubricant should strongly adhere to the rubbing surfaces (be adsorbed on them) and protect them from wear. In the case of destruction of the adsorbed film, it should react chemically with the metal surface, preventing seizure and welding.

It is very important that in prolonged operation at high temperatures and under the action of radiation, the lubricant retain its composition and properties and not form deposits tending to overheat the parts and contaminate the engine (or another mechanism) and not cause corrosion of the materials. Under any service conditions, the oil should be adequately pumped through the oil system and be sprayed in the zone requiring lubrication, when the oil is not delivered under pressure. One of the essential requirements placed on lubricants used in large quantities is the presence of a raw material and production base and a moderate cost of production [59, 70].

Requirements Placed on Properties

On the basis of general requirements, the following properties of lubricants are desirable:

- a) good lubricating capacity;
- b) the lowest possible viscosity, but sufficient to produce a reliable liquid layer in the components with hydrodynamic lubrication at the maximum operating temperature (not below the specified value at 50 and 100°C or any other value);
- c) a mildly sloping viscosity-temperature characteristic;
- d) a sharp increase in viscosity with rising pressure;
- e) antiseize properties at high loads;
- f) absence of unstable components separating in the form of contaminating deposits;
- g) absence or safe quantity of corrosive substances and components tending to be transformed into corrosive substances;

- h) low solidification temperature;
- i) high flash point of liquid oils (characterizing the stability to vaporization);
- j) narrow fractional composition of liquid oil;
- k) physical homogeneity (absence of mechanical impurities, water, and foaming tendency);
- l) minimum hygroscopicity;
- m) radiation resistance;
- n) absence of toxic substances [59, 70, 81].

Application of Requirements

Lubricants possessing a whole range of desirable properties are impossible to prepare in practice, since many of the requirements imposed on them are mutually contradictory. The selection of the properties of lubricants is even more of a compromise than that of the properties of fuels. Thus, aromatic hydrocarbons provide a high thermal-oxidative stability of petroleum oils but worsen the viscosity-temperature characteristic and increase the corrosiveness toward rubber. Paraffin hydrocarbons with a mildly sloping viscosity-temperature characteristic has a high solidification temperature. Natural carriers of lubricating capacity (organic acids, tars, sulfur compounds) worsen the thermal stability and increase the corrosive activity toward metals. Synthetic oils, which possess a number of valuable qualities, are corrosive and poisonous. For this reason, on each grade of oil are imposed stringent requirements with respect to the indices which are decisive, while less rigid requirements are set with regard to the remaining indices.

Certain properties of an oil can be controlled jointly in its daily use (for example, lubricating capacity, stability, corrosion properties). In order to narrow down these properties, indirect indices are used, i.e., values of density, ash content, coating capacity, acid number, flash temperature, etc. If the oil is in the range of norms with respect to the entire set of these indices, i.e., corresponds to a sample which has successfully passed government tests (on whose data the norms were established), it is assumed that the oil corresponds to it in chemical composition, and hence, in lubricating capacity, stability, and corrosive properties [59, 81].

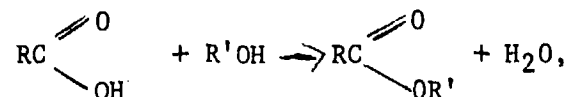
CHAPTER 7

OUTLINE OF PRODUCTION OF LUBRICANTS AND INDUSTRIAL LIQUIDS

PRODUCTION OF SYNTHETIC OILS AND LIQUIDS

Esters

Aviation synthetic oils are prepared from esters, which are products of the reaction of carboxylic acids with alcohols. The esterification reaction involves replacement of the hydrogen atom of the carboxyl group COOH in the acid molecule by a hydrocarbon radical of the alcohol, R';



where R is the hydrocarbon radical of the acid.

Oils are obtained by using mono- and dibasic high-molecular acids RCOOH and R(COOH)₂ and high-molecular alcohols with different numbers of hydroxyl groups ROH, R(OH)₂, R(OH)₃, R(OH)₄. They are prepared from petroleum products mainly by oxidizing unsaturated hydrocarbons, and also from plant raw material.

The most characteristic are the following catalytic esterification processes taking place at 140-225°C and atmospheric pressure:

a) preparation of diester (dioctyl sebacate) by reacting sebacic acid C₈H₁₆(COOH)₂, produced from vegetable castor oil, with isooctyl (2-ethylhexyl) alcohol C₈H₁₇OH;

b) preparation of glycol ester by reacting synthetic fatty acids

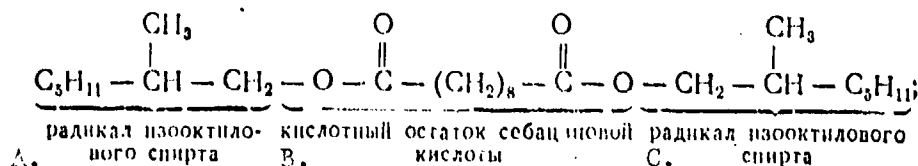
$C_5H_{11}COOH$, $C_6H_{13}COOH$ and others with the diatomic alcohol ethylene glycol

$C_2H_4(OH)_2$;

c) preparation of pentaerythritol ester by successively reacting synthetic fatty acids $C_5H_{11}COOH$, $C_6H_{13}COOH$ and others, first with methanol CH_3OH (primary esterification), and then with the tetraatomic alcohol pentaerythritol $C_5H_8(OH)_4$.

The catalysts used are ion exchange resins or zinc oxide. The esters obtained in these processes have the following molecular structure:

a) dioctyl sebacate:

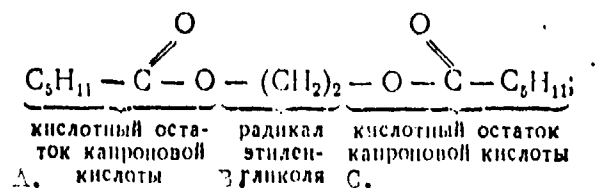


A. Isooctyl alcohol radical

B. Acid residue of sebacic acid

C. Isooctyl alcohol radical

b) Diethylene glycol ester of caproic acid:

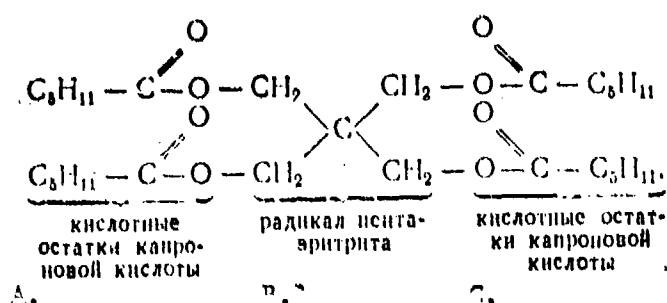


A. Caproic acid radical

B. Ethylene glycol radical

C. Caproic acid radical

c) pentaerythritol ester of caproic acid:



A. Acid residues of caproic acid

B. Pentaerythritol radical

C. Acid residues of caproic acid

Esters of other acids and alcohols can be similarly obtained [59, 70, 71].

Halo Derivatives of Hydrocarbons

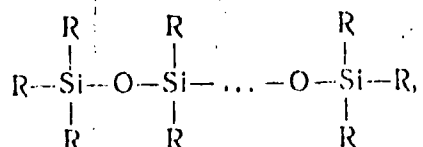
Fluorocarbon oils and liquids, which are products of complete fluorination of hydrocarbons (perfluorocarbons) $\text{F}-\text{C}(\text{F})_2-\text{C}(\text{F})_2-\dots-\text{C}(\text{F})_2-\text{F}$ have a much higher molecular weight and higher viscosity than the initial hydrocarbons. For this reason, low-viscosity fluorocarbon oils are obtained by fluorinating low-viscosity petroleum fractions - the kerosene and gasoline fractions, and oils of higher viscosity are obtained by fluorinating low-viscosity oil fractions.

Chlorofluorocarbon oils are produced by polymerization of chlorofluoroethylene: $\text{N}(\text{F}_2\text{C}=\text{CFCl}) \rightarrow (\text{F}_2\text{CFCl})_n$. The latter is obtained in two stages: first, methane is chlorinated and fluorinated, then its pyrolysis is carried out (partial decomposition of molecular structure under the influence of high temperature), which is associated with the formation of unsaturated molecules $(\text{C}_2\text{ClF}_3)_n$.

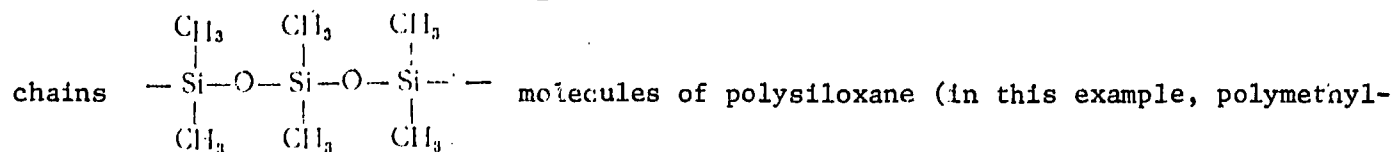
Fresons - low-molecular chloro- and bromofluoro derivatives of hydrocarbons, used as refrigerants and fire-extinguishing liquids (for example, tetrafluorodibromomethane - freon 114BR), are obtained by chlorinating and brominating hydrocarbons (methane, ethane, ethylene), then reacting the products with metal fluorides [59, 70].

Organosilicon Oils and Liquids

Polysiloxanes with the molecular structure



in the skeleton of which alternate silicon and oxygen atoms (R are hydrocarbon radicals, for example, CH_3 or C_2H_5), are produced in the final analysis from quartz sand, water and hydrocarbon gases. Reduction of silica SiO_2 forms pure silicon, which is treated with chloro derivatives of hydrocarbons, for example, chloromethane CH_3Cl . On reacting with water, the products of their combination, for example dimethyldichlorosilane $(\text{CH}_3)_2\text{SiCl}_2$, split off hydrogen chloride HCl and form the



siloxane). The length of the chains and their structure depend on the composition of the intermediate products - the chloro derivatives, and on the conditions of the processes and catalysts [59, 70, 71].

PRODUCTION OF PETROLEUM OILS

Vacuum Distillation of Fuel Oil

The initial product in the production of petroleum lubricants is fuel oil - the residue of petroleum distillation, consisting of high-boiling hydrocarbons. It is heated to 350-375°C and separated into fractions in a vacuum rectification column at a residual pressure of 40-50 Torr. To accelerate the process, superheated steam is introduced into the column; the hydrocarbons evaporate over the enormous surface area inside the steam bubbles.

In the upper section of the column is collected the solar distillate, which will be subjected to chemical processing and used in part to prepare diesel fuel and thickening oils; below are collected oil distillates from which are prepared oils for turbojet engines, MVP instrument oil, and transformer oil; from the middle section of the column are collected more viscous distillates of various industrial oils, lubricating oils, etc. If all the oil fractions are driven out of the fuel oil, a crude residue remains in the lower section of the column, if however only the low-viscosity fractions are distilled off, the undistilled residue (flux oil) - a mixture of viscous hydrocarbons with asphaltic tar substances - is used to prepare oils for aviation piston engines and transmission oils. Correspondingly, petroleum oils are usually divided into distillate and residual ones; the latter are marked by a high lubricating capacity [59, 72, 89].

Purification

To remove undesirable asphaltic tars, organic acids, and other impurities from oil distillates and the residue, the latter are subjected to purification.

The simplest acid-base purification is used in the production of transformer and other technical oils. It consists in treating the distillate with strong sulfuric acid (96-98%), then with alkali. The asphaltic tars, part of the naphthenic acids and heavy aromatic hydrocarbons tending to carbonize at high temperature readily react with sulfuric acid and are removed from the oil. Then the acid oil is treated with sodium hydroxide (caustic soda), which neutralizes the organic acids and sulfuric acid residue. To remove the residue of alkali and salts, the oil is washed with water and dried with heated air.

In the production of many aviation oils, use is made of acid contact (acid-earth) purification. It consists in treating the distillate or residue with sulfuric acid, then with bleaching earth (clay ground to a powder). When the latter comes in contact with hot acid oil, it adsorbs the asphaltic tars and waste of sulfuric acid purification on its enormous surface. The product is then passed under pressure through filters to remove the clay. Aviation oils purified in this manner are designated by the letters MK.

Selective purification, also used in the production of aviation fuels, is carried out by means of solvents, some of which dissolve only nonhydrocarbon impurities present in the distillate or residue, while others, on the contrary, dissolve only the hydrocarbons. Two layers are formed: a heavy extract - solvent containing the harmful substances being removed from the oil and a lighter layer - the refined (purified) oil with an admixture of the second solvent. They are separated and the solvents are driven off, to be used again. Aviation oils purified in this manner are designated MS.

It should be noted that the concept of "harmful" and "useful" oil components is somewhat arbitrary. Thus, tars, which tend to form carbon deposits and are

therefore considered harmful, simultaneously constitute carriers of the lubricating capacity of the oil. Oils subjected to excessive selective purification ("overrefined" oils) do not adhere to parts; this may result in increased wear and destruction of friction components. The high-viscosity, sticky, tarry mixture obtained after the selective solvent has been driven out of the extract is an excellent component for transformer oils operating under high dynamic load conditions at a comparatively low temperature.

If the oil fraction contains many asphaltic carbonaceous substances, their elimination requires a large consumption of sulfuric acid, selective solvents, etc. In such cases, preliminary deasphaltization of the oil intermediate is carried out: the latter is dissolved in light gasoline or liquid propane. The asphaltic carbonaceous and tarry substances, which are sparingly soluble in these solvents, precipitate out; after their removal, the solvent is distilled out of the oil [35, 59, 62, 72].

Deparaffinization

To obtain oils with a low solidification temperature, the purification is carried out by removing the high-melting paraffin hydrocarbons. The oil is dissolved in ligroin or liquid propane, or in some other low-freezing solvent. The solution is cooled to a temperature of minus 25-40°C and delivered to high-speed centrifuges, where the solidified hydrocarbons separate from the oil under the influence of centrifugal forces. The mixture of solid paraffins with a certain amount of liquid oil and impurities is called petrolatum, from which are obtained solid white paraffin and ceresin (a dark mixture of various solid hydrocarbons). All three products are used in the preparation of protective lubricant greases. Recently, instead of the expensive and complicated deparaffinization by cooling,

carbamide purification analogous to the corresponding purification of fuel has been introduced [59].

PREPARATION OF ADDITIVES

Viscous Additives

Thickeners for the preparation of oils and industrial liquids with a low-viscosity base are obtained by catalytic polymerization. Polyisobutylene is obtained by polymerization of the gaseous unsaturated hydrocarbon isobutylene, which is isolated from petroleum refining gases: $nC_4H_8 \rightarrow (C_4H_8)_n$. Polyisobutylene of rubberlike consistency with an average molecular weight of about 20,000 is produced, possessing a high thickening capacity, but insufficiently stable to depolymerization, is produced, along with the more stable octol-600, which is a viscous liquid ($\gamma_{100} \approx 600$ cS). Polymethacrylates are made by esterifying the unsaturated methacrylic acid C_3H_5COOH (obtained from acetone and prussic acid) with a mixture of high-molecular alcohols $C_{12}H_{25}OH - C_{18}H_{37}OH$. The ester obtained is subjected to polymerization. "Vinipol" $(C_2H_3OC_4H_9)_n$ (polymer of vinyl-n-butyl ester) is synthesized from acetylene C_2H_2 and normal butyl alcohol C_4H_9OH with the participation of acetic acid [42, 59, 70].

Antioxidant and Anticorrosive Additives

An antioxidant action is manifested chiefly by phenolic compounds. Phenol C_6H_5OH and the analogous bicyclic compound naphthol $C_{10}H_7OH$ are obtained from sulfonic acids formed during the sulfuric acid purification of oils and fuels, and are also isolated from coal tar. Their derivatives are obtained by alkylation

(addition of alkyl groups C_nH_{2n-1}), treatment with amines, etc. The following additives are thus produced (which are solid at room temperature): dibutylcresol (DBK-69, Ionol, topanol "O") $CH_3C_6H_2OH(C_4H_9)_2$, diphenylamine $(C_6H_5)_2NH$, parahydroxydiphenylamine $C_6H_5NHC_6H_5OH$, penyl- α -naphthylamine $C_6H_5NHC_{10}H_7$.

An anticorrosive action is exhibited by heterocyclic amino-derivative sulfur-containing compounds - phenothiazine (thiodiphenylamine) $C_6H_5<\begin{smallmatrix} S \\ NH \end{smallmatrix}>C_6H_5$ and mercaptobenzothiazole $C_6H_5<\begin{smallmatrix} S \\ N \end{smallmatrix}>CSH$ [37, 59, 70].

Antiwear and Antiseize Additives

A decisive role in the antiwear and antiseize action of additives is played by phosphorus, sulfur and chlorine introduced into the composition of the organic molecules. Tricresyl phosphate and triphenyl phosphate are formed from phosphoric acid and cresol or phenol respectively; they have an ester structure $(CH_3C_6H_4)_3PO_4$ and $(C_6H_5)_3PO_4$. "Sovol" is obtained by chlorinating benzene and constitutes a mixture of pentachlorophenyl C_6HCl_5 and tetrachlorophenyl $C_6H_2Cl_4$. Sulfured octol is obtained by adding 1-2% of sulfur in the course of polymerization of isobutylene, so that an admixture of sulfides of the type $R-S_n-R'$ (where R and R' are alkyl radicals) is formed in polyisobutylene. Mercaptobenzothiazole also belongs to this type of additives [59, 67, 70].

PRODUCTION OF LUBRICATING GREASES

Preparation of Soap Lubricants

Lubricating greases are usually prepared by thickening petroleum or synthetic oils with soaps or solid hydrocarbons (other thickeners are also used for certain lubricants). The main type of thickeners - soaps - are compounds obtained by

reacting metals with high-molecular fatty acids (stearic and others). The most common lubricants based on lithium, sodium and calcium soaps are obtained in digesters by direct saponification of fatty acids or fats with the corresponding alkali - a solution of lithium hydroxide LiOH , sodium hydroxide NaOH , or milk of lime Ca(OH)_2 . To achieve a better dispersion of the soap, part of the oil is introduced at once into the digester. Saponification is carried out at $80-90^\circ\text{C}$ for several hours. Then the remainder of the oil is added; in the case of preparation of lithium and sodium lubricants, the temperature is raised to approximately 200°C . The heating is continued until the soap is completely dissolved in the oil. The lubricant is cooled according to predetermined conditions on which the structure of the soap skeleton and quality of the lubricant depend.

Zinc, aluminum, and many other lubricants are prepared from finished soaps; soap prepared in advance is immersed in the digester in an oil heated to $150-210^\circ\text{C}$ (depending on the type of lubricant). Stirring causes the fine soap particles to break up in the oil and on cooling to form a structural skeleton whose cells hold the oil [17, 59].

Preparation of Hydrocarbon Lubricants

Lubricants which do not contain soaps - gum lubricant, vaseline and certain others - are obtained directly from fuel oil during the production of oils or are prepared by dissolving hydrocarbons (paraffin, ceresin) in oil.

Certain grades of lubricants after cooling are subjected to mechanical homogenization (equalization of microstructure) on a grinding machine. The process of preparation of the lubricant at atmospheric pressure lasts from 10-12 hours to

several days. In autoclaves at a pressure of 5-8 atmospheres, the time required for the preparation of certain lubricants is substantially reduced [59].

PRODUCTION OF ETHANOL

Alcohol from Plant Raw Material

The plant raw material for ethanol production are food products (grain, potatoes, beet sugar syrup) wood and plant waste, and waste from sulfite digestion of cellulose (sulfite liquor). Alcohol is formed as a result of fermentation of sugary substances. The latter are obtained by processing starch present in food raw material, or by hydrolysis of plant cellulose. From food raw material, 88% raw alcohol is directly produced, and from hydrolysis or sulfite digestion of cellulose - 94-95% industrial (hydrolysis or sulfite) alcohol. Impurities are separated by distillation, and 95.5% rectified alcohol is obtained.

The consumption of starting products per ton of food alcohol is around 4.5 tons of grain or 14 tons of potatoes. The production of food alcohol has decreased in the last few years. Double-rectification hydrolysis alcohol is equal in quality to food alcohol [59, 72].

Synthetic Alcohol

Ethyl alcohol is being produced on a steadily increasing scale by synthesis from ethylene, which is evolved from a mixture of petroleum refining cracking gases. It is 2-2.5 times cheaper than alcohol from vegetal raw material, but because of the presence of impurities that are difficult to remove, its quality is lower.

The alcohol is obtained by direct hydration of ethylene $C_2H_4 + H_2O \rightarrow C_2H_5OH$, which takes place at $250^\circ C$ at a pressure of 60-100 atmospheres with a catalyst, or by indirect hydration (ethyl esters of sulfuric acid are obtained and subjected to hydrolysis) [59, 72].

CHAPTER 8

OILS FOR AIRCRAFT ENGINES

CONDITIONS OF OPERATION OF OIL IN TURBOJECT ENGINES AND REQUIREMENTS PLACED ON THEIR OILS

Lubrication System

A typical lubrication system for modern TJE is an open circulation system in which the oil is taken from the oil tank, and after each circulation cycle returns to the tank (Fig. 45). The oil is supplied to the lubricated parts by a delivery pump through a fine filter along high-pressure lines (marked by thick lines in Fig. 45). The main such parts are antifriction bearings of the compressor and turbine, operating at speeds of the order of 6000-12,000 rpm. The oil is delivered to the bearings into the cage by three or four jet nozzles, is finely sprayed, coats the surface of the antifriction elements, rings, and cages, washes the outer surface of the bearings, and, highly foamed, flows down into sumps, whence it is sucked up by scavenging pumps. To prevent cavitation in the scavenging lines (thick dashed lines in Fig. 45), excess pressure (of the order of 0.1-0.3 atm of excess pressure) is produced in the oil cavities. The compressed air leaks in from the outside through seals of the oil cavities, and thus prevents leakage of the oil.

Scavenging pumps force the oil through a centrifugal gas separator which breaks up the foam, then through a radiator and into an oil tank, which in supersonic aircraft is cooled by the fuel, and in subsonic ones, by air. The oil tank and all the oil cavities reached by air, including the cavity of the centrifugal gas separator, are connected by lines (light lines in Fig. 45) to a centrifugal blower,

and after passing through it, escapes into the atmosphere. The blower separates most of the oil suspended in air and returns it to the oil system.

Typical data on oil pumping and temperature conditions in various sections of the lubrication system are given in Fig. 45. Normal operation of TJE is obtained with a small amount of oil (10-25 l) circulating actively in the system (50-130 times per hour, i.e., the duration of one cycle is 0.5-1 min). Because of the diversity of service conditions, the oil temperature (in the volume) may vary over a wide range from minus 30-60°C to plus 130-150°C and higher. For this reason, a mildly sloping viscosity-temperature characteristic of the oil and a low solidification temperature of the latter are necessary. The compressor bearings heat up to approximately 120-200°C during their operation, the turbine bearings heats up to 250-300°C, and after the engine stops, because of the cessation of oil circulation and external blowing on the housing of the bearings, to much higher temperatures (the heating dynamics of the turbine bearing are shown in Fig. 46; the relatively moderate ring temperature shown in this figure corresponds to a subsonic engine). Heating of the bearings promotes vaporization of the oil and creates conditions for oxidation, sedimentation and lacquering. This results in requirements for a low vaporizability and high thermal oxidative and thermal stability.

In addition to the rotor bearings, the oil lubricates the gear transmissions of units operating at moderate loads. To some of these, oil is also supplied by jet injectors, while the others are lubricated by the oil mist formed in the gear box [31, 59, 71].

Рис. 45. Свойства смазочного масла, влияющие на эксплуатационную надежность газотурбинной силовой установки

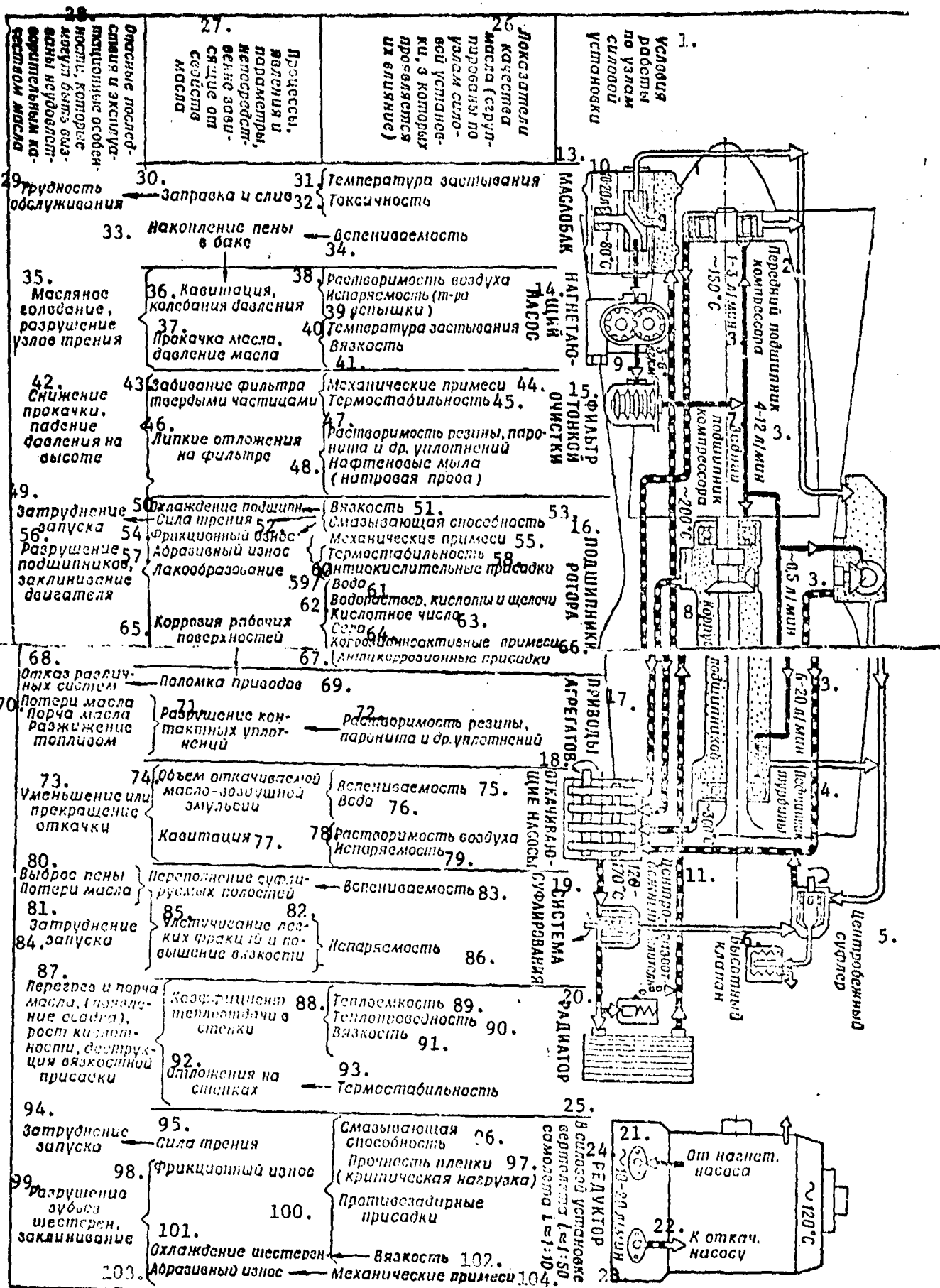


Fig. 45. Properties of lubricating oil affecting the operational reliability of a gas turbine power plant.

Caption for Fig. 45

Fig. 45. Properties of lubricating oil affecting the operational reliability of a gas turbine power plant. Key:

1. Operating conditions in the power plant components; 2. Front bearing of compressor; 3. 1/min; 4. Turbine compressor; 5. Centrifugal blower;
6. Height value; 7. Rear bearing of compressor; 8. Housing of bearings;
9. kg/cm²; 10. 10-20 l; 11. Centrifugal gas separator; 13. OIL TANK;
14. PRESSURE PUMP; 15. FINE PURIFICATION FILTER; 16. ROTOR BEARINGS;
17. UNIT DRIVES; 18. WITHDRAWAL PUMPS; 19. BLOWER SYSTEM; 20. RADIATOR;
21. From pressure pump; 22. To withdrawal pump; 23. 1/min; 24. REDUCTION GEAR;
25. In power plant of helicopter, $1 \approx 1:50$, and of airplane, $1 \approx 1:10$;
26. Oil quality indices (grouped according to components of power plant in which their influence is manifested); 27. Processes, phenomena and parameters directly dependent on oil properties; 28. Dangerous aftereffects and performance characteristics which may be caused by unsatisfactory oil quality; 29. Servicing difficulty; 30. Filling and draining; 31. Solidification temperature; 32. Toxicity; 33. Accumulation of foam in tank; 34. Foamability; 35. Oil deficiency, failure of friction components; 36. Cavitation, pressure fluctuations; 37. Oil transfer, oil pressure; 38. Solubility of air; 39. Vaporizability (flash temperature); 40. Solidification temperature; 41. Viscosity; 42. Decrease in rate of flow, pressure drop at altitude; 43. Clogging of filter with solid particles; 44. Mechanical impurities; 45. Thermal stability; 46. Sticky deposits on filter; 47. Solubility of rubber, Paronit and other seals; 48. Naphthenic soaps (sodium test); 49. Difficult starting; 50. Cooling of bearing; 51. Viscosity; 52. Friction force; 53. Lubricating capacity; 54. Friction wear; 55. Mechanical impurities; 56. Failure of bearings, jamming of engine; 57. Abrasive wear; 58. Thermal stability; 59. Lacquering; 60. Antioxidant additives; 61. Water; 62. Water solution, acids and alkalis; 63. Acid number; 64. Sulfur; 65. Corrosion of working surfaces; 66. Corrosive impurities; 67. Anticorrosive additives; 68. Failure of various systems; 69. Breaking of drives; 70. Oil losses, oil spoilage, dilution with fuel; 71. Destruction of contact seals; 72. Solubility of rubber, Paronit and other seals; 73. Decrease or interruption of scavenging; 74. Volume of oil-air emulsion being scavenged; 75. Foamability; 76. Water; 77. Cavitation; 78. Solubility of air; 79. Vaporizability; 80. Foam ejection; 81. Oil losses; 82. Overfilling of blown cavities; 83. Foamability; 84. Difficulty in starting; 85. Volatilization of light fractions and increase in viscosity; 86. Vaporizability; 87. Overheating and spoilage of oil (appearance of sediment), increase in acidity, degradation of viscosity additive; 88. Coefficient of heat transfer to the walls; 89. Heat capacity; 90. Thermal conductivity; 91. Viscosity; 92. Deposits on walls; 93. Thermal stability; 94. Difficulty in starting; 95. Friction force; 96. Lubricating capacity; 97. Strength of film (critical load); 98. Friction wear; 99. Destruction of gear teeth, jamming; 100. Antiseize additives; 101. Cooling of gears; 102. Viscosity; 103. Abrasive wear; 104. Mechanical impurities.

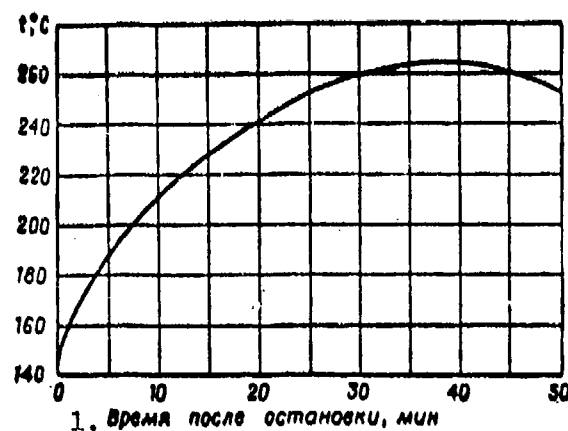


Fig. 46. Change in the temperature of the outer race of a turbine bearing after the engine stops. Key:

1. Time after halt, min

Friction Components

In the rotor bearings, the contact stresses reach $20,000\text{--}30,000\text{kg/cm}^2$. They are absorbed by the oil boundary film. The oil should have a sufficient lubricating capacity so that in the course of the several microseconds during contact between the rolling bodies with rings at each point the film is not destroyed. In parts under a smaller load (at the ring ribs and cage saddles), liquid friction usually takes place. In view of the high speeds, a high oil viscosity is not required to produce liquid friction, and from the standpoint of delivery to the bearings and their cooling, low-viscosity fuel is unquestionably desirable [30, 92, 112].

Action on the Lubrication System

During the operation of TJE, oil comes in contact with catalytically active copper alloys (bronze or brass bearing cages), with corrosion-sensitive lead and

other coatings, and partly soluble or swelling sealing materials (rubber, Paronit). The more neutral is the oil toward them, the longer the service life of the engine and of the oil itself. In TJE, oil is not in direct contact with the products of fuel combustion and with the liquid fuel (provided of course that the fuel-oil radiators and seals of the fuel pump drive are operating properly).

The oil properties which may affect the operational reliability of TJE are grouped in Fig. 45 according to the components in which this influence is manifested; the processes and phenomena dependent on the properties of the oil and the associated service characteristics and possible dangerous aftereffects of an unsatisfactory oil quality are indicated [37, 71, 91, 112].

SYNTHETIC OILS FOR TURBOJET ENGINES

SERVICE CHARACTERISTICS OF MODERN GRADES

Synthetic diester and polyester oils with antioxidant and antiwear additives are used as the main grades in high temperature TJE of supersonic aircraft. These oils are considerably better than petroleum oils from the standpoint of the viscosity-temperature characteristic and low-temperature properties, lubricating capacity, and, what is particularly important, they are thermally stable, and for all practical purposes do not evaporate even under the operating conditions of heat-stressed modern engines, so that they can be used without change during the entire service life of the engine. VNII NP-50-1-4F oil is efficient up to approximately 175°C. At a higher temperature, it is insufficiently stable in a thin layer. Oil 36/1 is efficient to an even higher temperature, of the order of 200°C, and for a short time even up to 250°C.

Molecules of diester and polyester oils contain two or more polar groups

- $\text{C} \begin{array}{l} \nearrow \text{O} \\ \searrow \text{O} \end{array}$ -, which ensure their orientation at the metal surface and the formation

of an adsorbed lubricating film based on the oil itself (in contrast to petroleum oils, where the carriers of lubricating capacity are admixtures of acids, resins, etc.). This turns out to be important at the high operating temperature of bearings, when the boundary film formed by the purified petroleum oil is destroyed by the loads acting on it. The strength of a boundary film of synthetic oils, estimated from the critical load before its destruction, is twice as high as the strength of a film of petroleum oils used in TJE.

The viscosity of VNII NP-50-1-4F oil at 100°C is no less than 32. cS, and that of 36/1 oil is slightly higher, no less than 3.5cS. The viscosity-temperature characteristic of both oils have a sufficiently mild slope (Fig. 47), and the solidification temperature is below -60°C. If starting of TJE with a starter of standard power up to a maximum oil viscosity of 3000-4000 cS is considered possible, then such oils should provide for starting down to minus 40-50°C without preheating. The change in the viscosity and low-temperature properties after a long operation of the oils is insignificant if the temperature limit of their efficiency has not been exceeded.

Owing to their low vaporizability, the consumption of synthetic oils amounts to only a fraction of that of petroleum oils. It is evident from the data given in Fig. 48 (right) that the vaporization of a diester oil in a thin film only begins virtually at the same temperature at which petroleum oils, whose viscosity in the operating temperature range is similar, vaporize almost completely.

An important drawback of synthetic oils is the swelling of the rubber hoses and seals, made of ordinary grades of rubber, which are in contact with them. Special grades of rubber are required to make the rubber parts of an oil system. Some coatings of nonferrous metals able to withstand contact with petroleum oil are attacked by synthetic oils; therefore, in engines designed for synthetic oils, the coatings are made only of materials compatible with the oils. Prolonged action of a synthetic oil may damage the electric wiring insulation and other elements of the external framework of the engine, and they are therefore coated with oil-resistant varnishes, and the cleanliness of the external surfaces of the engines is carefully maintained [1, 37, 59, 65, 71, 96, 105].

Action of Additives

An antiwear additive (tricresyl phosphate or mercaptobenzothiazothiazole) provides for a rapid running-in of friction components on synthetic oil, decreases their wear, and in the presence of deviations from normal conditions or malfunctions leading to dangerously high loads or oil deficiency, prevents galling. An antioxidant additive (tenths of a percent) extends the service life of synthetic oils to the total engine service life, this being very important in view of their high cost and scarcity. Because of the toxicity of the additives, safety measures must be observed in work with synthetic oils. It is necessary to operate only in uniform (overalls, coveralls, apron). Care must be taken to prevent the oil from reaching the eye or the skin, and the hands should be coated with a special film-forming paste. There must be no eating, drinking or smoking near the work stations; before a meal, the uniform should be taken off, and the hands thoroughly washed with soap and hot water. If oil happens to fall on the skin, clothing, tools, or outer surfaces of the engine, it should be removed with a rag dipped in kerosene, then the skin and clothing should be washed with soap and water [37, 59, 71, 96].

Foreign Grades

The chief foreign producer of aviation oils is the Shell Co. It supplies oils to the aviation of the USA, Britain, and most western European countries. The diester synthetic oil Turbooil-300 produced by this company (earlier called Turbooil-15), or Aeroshell-300 with a viscosity of about 3.0-3.5 cS at 100°C, is used for many types of TJE of supersonic aircraft (the company's numerical designation of synthetic oils corresponds to the viscosity in cS multiplied by 100, at a temperature of 210°F, i.e., 98.9°C). The oil base is usually diisooctyl sebacate. The oil contains over 5% of additives (antiwear, antioxidant, anti-foam). Its solidification point is no higher than -59°C, and the viscosity at -54°C is no greater than 13,000 cS. Similar in composition and properties are the oils Castrol-3C (produced by the Anglo-American company Castrol Ltd.) and Air-3513 (French manufacture). The temperature limit of the use of these oils is 175-180°C, and for short periods of time, up to 240°C. Viscous diester oil Turbooil-750, which is the same for TJE and TPE, is used in certain TJE (in particular, British ones).

Other thermally stable oils produced for TJE are polyester oils of various compositions and mixed (di- and polyesters) operating at temperatures up to 200-210°C and tolerating heat for short periods up to 260°C. They include, for example, Castrol-205 oil [37, 59].

PETROLEUM OILS FOR TURBOJET ENGINES

Grades

Lubrication of TJE and subsonic and transonic aircraft as well as certain types of supersonic aircraft with a Mach number no greater than 1.5-2 involves the

use of low-viscosity petroleum oils for selective purification MS-6 and oxygen-contact purification MK-6 and MK-8 (the latter was the chief grade for a number of years, and is now regarded as a substitute in most engines). In addition, transformer oil is allowed for use as a substituent in certain engines. In TJE of aircraft with $M \approx 2$, in particular, those where synthetic oils are used as the main grades, MK-8P oil may be used (with an antioxidant additive); its service life is limited by the thermal stress of the engine [1, 37, 59, 71].

Viscosity and Starting Properties

The number of the brand of the above grades of petroleum oils denotes the viscosity of 50°C. The viscosity of MK-6 and MS-6 oils at this temperature should be between 6.0 and 6.3 cS, and that of MK-8 oil, not below 8.3 cS; it is shown in Fig. 47 over a wide temperature range. Low-paraffin crudes are used in the manufacture of these oils, or an extensive deparaffinization is carried out; a low solidification temperature of the oils is thus achieved - not above -60°C for MK-6 and not above -55°C for MK-8 and MS-6. MS-6 and MK-6 oils have better starting properties than MK-8, similar to the starting properties of synthetic oils. Their advantages are even greater after prolonged operation in TJE. These oils have a narrower fractional composition than MK-8 oil (Fig. 48). Their ordinary boiling range is about 60°C (from 320 to 380°C in vacuum), whereas for MK-3, it is approximately 180°C (from 260 to 440°C). They contain a smaller quantity of easily vaporizing fractions (as indicated, in particular, by a higher flash point - not below 140°C versus 135°C for MK-8 oil) and a smaller amount of heavy viscous fractions, which could decrease the starting properties of the oil as the light fractions are lost. This makes it possible to start the engine without preheating, approximately down to -40°C during the entire established service life. Fresh MK-8 oil provides for cold starting of TJE approximately down to -35°C, and

after 100 hours of operation of TJE, its viscosity at -40°C increases 4-5-fold due to evaporation of light fractions (Fig. 49), causing difficulty in starting a cold engine at temperatures below minus $25-30^{\circ}\text{C}$ [1, 2, 37, 59].

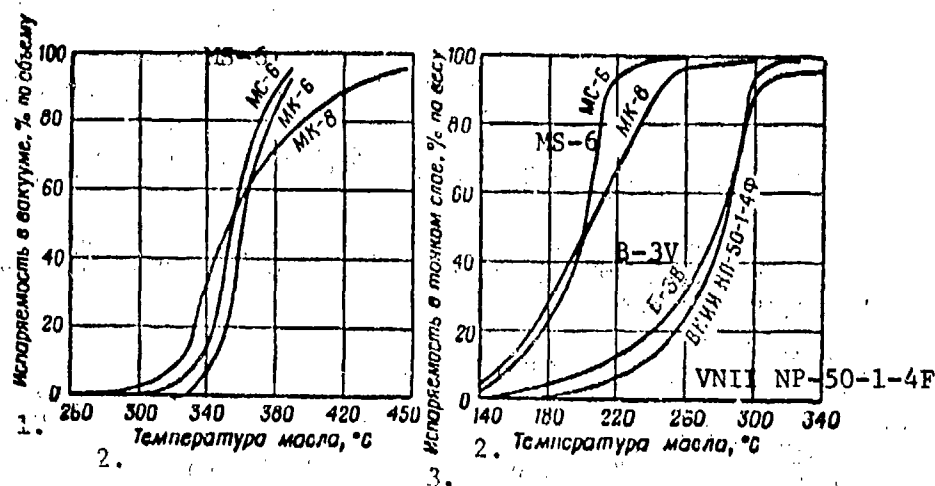


Fig. 48. Vaporizability (fractional composition) of certain petroleum and synthetic oils. Key:

1. Vaporizability in vacuum, % by volume; 2. Oil temperature, $^{\circ}\text{C}$; 3. Vaporizability in thin layer, % by weight.

Effect on the Engine

In lubricating capacity, all three grades of petroleum oils for TJE are approximately equivalent. The critical load on the lubricant film which they form is not high, 28-30 kg (see Fig. 40) according to tests on the four-ball tester. This is adequate under the temperature conditions of bearings typical of subsonic TJE. At higher temperatures characteristic of bearings of supersonic TJE, the adsorption bond between the boundary film and the metal weakens, the lubricant film breaks down during the operation of the bearings, and their wear increases. In petroleum oils for TJE, a significant content of natural carriers of lubricating capacity (oxygen- and sulfur-containing compounds, resinous substances, etc.) is not allowed, since they are the chief sources of deposits and corrosion under high temperature conditions.

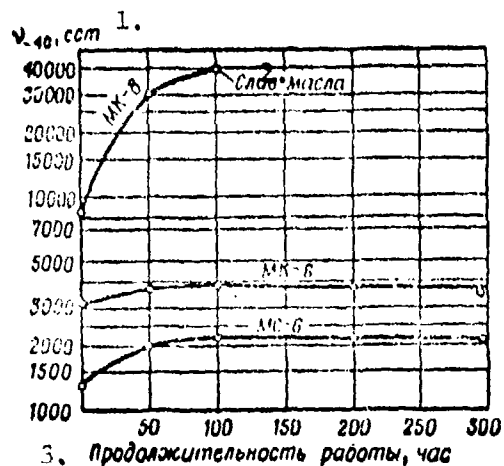


Fig. 49. Change in viscosity at -40°C in the course of prolonged operation of oils in TJE. Key:

1. cS; 2. oil drainage; 3. Duration of operation, hr.

The stability of petroleum oils in TJE depends on the conditions of their use. Oxidation and contamination of petroleum oil in subsonic and transonic TJE usually take place so slowly that for all practical purposes they do not determine its service life in the engine. In most types of such TJE, the oil is changed after 100-200 hours or more. However, in supersonic TJE at an oil temperature in the bearing zone up to $150-200^{\circ}\text{C}$ or higher, the thermal oxidative stability of petroleum oils turns out to be insufficient: dense lacquer deposits are formed on the surfaces of bearings, and the oil lines and injectors become clogged with carbon deposits.

The MK-6 and MS-6 oils are somewhat more stable than MK-8, since they contain a smaller amount of unstable hydrocarbons. MS-6 oil is inferior to MK-6 oil, since it contains almost no slightly branched polycyclic hydrocarbons, which on oxidation form phenolic compounds, which are natural antioxidants. To ensure the thermal oxidative stability of MS-6 oil, an antioxidant additive, dibutyl cresol (lonol), is added in the amount of 0.2% [37, 71].

Improved Oils

Oil based on MK-8, designed for thermally stressed engines, is designated MK-8P. It contains 0.6% of dibutyl cresol (ionol). The consumption of the additive during service of the oil in the engine depends on the thermal regime and other factors initiating oxidation reactions in the oil; in some thermally stressed engines, the oil may operate for not more than 25 hours, and in others, for up to 50 hours.

In view of the scarcity of synthetic oils and unsatisfactory service qualities of pure petroleum oils, special "intermediate" oils have been developed which have a low-viscosity petroleum base, for example, MS-6, but contain 10-12% of additives (polymers, phenols, compounds of sulfur, phosphorus, chlorine, nitrogen), which increase the viscosity, lubricating capacity, and thermal stability [37, 59].

Transformer Oil

At a temperature of air near the ground not below -30°C , the use of transformer oil is also allowed in certain types of engines. Its use for lubricating TJE goes back to the initial period of introduction of jet engine technology into aviation, when oils specifically designed for TJE had not yet been developed. It is similar in most properties to grade MK-8, but is inferior to it in starting properties and stability [65].

Foreign Grades

In the USA, Great Britain and several western European countries, use is made of 1010 oil (or Turbooil-2), having a viscosity not below 2.5 cS at 99°C , and

1005 oil (Turbooil-1) of lower viscosity, specially designed for Arctic conditions. They are labeled according to viscosity in cS at 100°F (38°C) by adding the number 1000 [37, 70].

PROSPECTIVE LUBRICANTS FOR TJE WITH UNUSUALLY HIGH TEMPERATURES OF FRICTION COMPONENTS

Hydrocarbon Oils

The temperature of the friction components of TJE aircraft with Mach number 3 in the near future is expected to be of the order of 300-400°, and for M=3.5-4 450°-600°C, which will require a considerable increase in the thermal stability of the oils.

Studies carried out abroad indicate the possibility of obtaining oils for friction components with a temperature of 300-350°C, which surpass ester type synthetic oils in thermal oxidative and thermal stability, from readily available and cheap petroleum crude. The methods of preparation of these oils include high refining and hydrogenation of narrow petroleum fractions, as well as chemical processing of unsaturated and aromatic hydrocarbons obtained from the crude in the course of fuel production, and a mandatory introduction of a set of additives. The loss of carriers of lubricating capacity due to high refining plays no part in the introduction of effective antiwear additives into the oil. The oil composition should be chosen so that it has a high "response" to anti-oxidant additives [37, 70].

Fluorine- and Chlorine-Fluorine-Containing Oils

Among synthetic oils, fluorocarbon oils are considered to be the most stable at high temperatures. They are fundamentally unable to oxidize, since fluorine,

which is the strongest oxidant, forms a stronger bond with the carbon of the molecules than oxygen. They are noncombustible and chemically inactive, i.e., do not cause corrosion, are not affected by corrosive components, and are non-toxic. Fluorocarbon oils have a high heat resistance and do not form sediments up to 450°-500°C. Their lubricating capacity is good. An important disadvantage of these oils is a very steep viscosity-temperature characteristic. For this reason, fluorocarbon oil selected for operation at high temperatures may turn out to be unsuitable not only at low but also at moderate temperatures.

A somewhat better viscosity temperature characteristic but lower thermal stability is displayed by chlorofluorocarbon oils. They are stable only up to 300-360°C, but do not form a carbon sediment on decomposing under higher temperature conditions. Their lubricating capacity is very good, and their corrosiveness toward most metals (except copper) is nil. An important quality of these oils is their resistance to highly corrosive components or rocket propellants and to liquid oxygen, and their nonignitability, which permits their use for lubricating turbopump units of LPRE. When they fall on the skin, the oils have an irritant effect.

A very good viscosity-temperature characteristic combined with thermal stability is displayed by organosilicon oils, but they have a poor lubricating capacity. As high-temperature oils, hybrid compounds prepared from them have been proposed, i.e., organosilicon fluoroesters, combining the chief advantage of organosilicon liquids (a mildly sloping viscosity-temperature characteristic) and fluorocarbon compounds [37, 59, 70].

Melts of Metals and Glass

The expected rise in the operating temperatures of TJE friction components in the near future will probably continue, thus eliminating even the most thermally stable organic and heteroorganic liquids. The types of lubricants fundamentally possible under these conditions are melts of metals and glass, solid (dry) lubricants and gases.

Liquid metals have qualities which are important for lubricants, i.e., a very high thermal conductivity which facilitates heat transfer from rubbing surfaces, a very mildly sloping viscosity-temperature characteristic, and a wide liquid-state temperature range. The chief difficulties interfering with their application is oxidation with air with the formation of solid oxides (powders, films) and a high crystallization temperature. Mercury, which is liquid at room temperature, is unsuitable, because its boiling point is too low (367°C at atmospheric pressure). If preheating is present, use may be made of low-melting, oxidation-resistant gallium, indium and their alloys. The melting point of gallium is 30°C, and the metal has a tendency to supercool. Indium melts at 155°C; it is a soft metal at room temperature (despite its high density, 7.3). It has long been used as an antifriction coating in aviation bearings. Both gallium and indium do not vaporize up to very high temperatures (the boiling point of indium is 1450°C, and that of gallium, 2070°C).

Of interest may be the simultaneous use of low-melting alkali metals as lubricants in nuclear power plants of flying vehicles where they are used as the heat carrier or as the source of the working substance. The melting point of cesium is 28.5°C, potassium 62°C, sodium 97.5°C, and the melting point of their eutectic alloys is still lower: that of an alloy of 76% potassium and 24% cesium, -48°C, and 77% potassium and 23% sodium, -12°C. Their boiling points are high (cesium

self-ignites in air) and decompose water with the evolution of hydrogen, which ignites immediately when water comes in contact with cesium and potassium.

Ideally resistant to oxidation by a liquid lubricant may be molten glass, since it is a mixture of oxides of silicon SiO_2 , boron B_2O_3 , and metals. Relatively low-melting compositions are sought which possess the required lubricating capacity in liquid form [37].

Solid (Dry) Lubricants

A solid substance can fulfill the functions of a lubricant if it has a layered microstructure with weak interplanar bonding and is capable of being adsorbed on rubbing surfaces.

Graphite has been known for a long time as a solid lubricant. The distance between the plane layers of its crystals is almost three times as great as between the atoms within the layers, and bonding between the layers is easily achieved by active electrons; graphite splits quite well along its layers. Flat plates of graphite adhere strongly (are attracted by electrostatic forces) to steel, cast iron, chromium, and less strongly to copper and aluminum (this depends mainly on the character of the oxide films on the metal surface). A solid graphite lubricant in contact with undried air gives a coefficient of sliding friction of 0.04-0.08. The latter increases sharply with decreasing air pressure and decreasing humidity, including high altitude conditions and vacuum (oxygen and water molecules apparently weaken the interplanar bonds of graphite). The friction coefficient also increases with the load and rising temperature, especially above 600°C ; this temperature is usually considered to be the efficiency limit of solid graphite lubricant. The high thermal conductivity of graphite, due to free "metallic"

electrons, promotes heat transfer from the shear planes and preservation of the strength of the lubricant layer.

In recent years, molybdenum disulfide MoS_2 , a bluish-gray powder with a metallic luster, has been increasingly used abroad as a solid lubricant. It has a layered crystal structure: the distance between sulfur atoms located in different crystal layers is almost four times the distance within the layers. The coefficient of friction for lubrication with molybdenum disulfide under ordinary atmospheric conditions is approximately the same as that of graphite (0.05-0.095). However, with rising load and temperature, decreasing humidity, and lowering of the air pressure down to a vacuum, the coefficient does not increase, as in the case of graphite, but decreases by a factor of two to three. This is very valuable for high-load friction components and high-altitude conditions. The effect of air and moisture is related to the relatively high chemical reactivity of molybdenum disulfide: its reaction products with water and oxygen have a higher friction coefficient. The supporting power of the boundary lubricant film of molybdenum disulfide is higher than that of any lubricating oils. In contact with air, molybdenum disulfide can be used up to approximately 450°C (it oxidizes rapidly at higher temperatures), and in a vacuum, approximately up to 1100°C ; its melting point is 1185°C . It is not decomposed by strong radiation.

In the view of foreign experts, of interest as dry lubricants are copper phthalocyanines $\text{C}_{32}\text{H}_{16}\text{N}_6\text{Cu}$, iron phthalocyanines $\text{C}_{32}\text{H}_{16}\text{N}_8\text{Fe}$, and other phthalocyanines - light or dark blue powders used in the manufacture of textile dyes. These are metal-containing polycyclic organic compounds with large planar molecules. Possessing weak intermolecular bonds (and thus a low resistance to shear), they form chemical bonds with a metal surface.

The phthalocyanine film is held on the contact surfaces of antifriction bearings up to 650°C. The coefficient of sliding friction of phthalocyanines at temperatures up to 300-400°C is higher than that of graphite and molybdenum disulfide, but as the temperature rises to 500°C, it decreases severalfold, approximately to 0.03-0.05 (in contact with air). Phthalocyanines are marked by a thermal stability unusual for organic compounds, i.e., up to a temperature of about 700°C, and by resistance to neutron and gamma irradiation [12, 70].

Gaseous Lubrication

The use of air and other gases for lubricating friction components is very tempting because of their low dynamic viscosity, approximately 1000 times lower than the viscosity of oils at high operating temperatures of TJE friction components. Friction in the presence of complete separation of the surfaces by the gas layer is correspondingly lower. As the temperature rises, the viscosity of gases, in contrast to that of liquids, increases as a result of reinforcement of molecular exchange between neighboring layers (at the same time, the braking or accelerating influence of one layer on another is enhanced). The higher the temperature, the worse the lubricant layer of the liquid and the better and more reliable the gaseous layer.

The principle of operation of sliding bearings on a gaseous lubricant may be aerostatic - a gaseous "cushion" is created which supports the shaft even when it does not rotate and aerodynamic - the gas is drawn by the rotating shaft into a wedge-shaped clearance and pushes the shaft away from the surface of the bearing. At high temperatures, air and certain other gases may cause the surface to corrode. In a gas-static bearing, the corrosion does not affect its operation. In a gas-dynamic bearing, the film of the reaction products of the gaseous lubricant with the metal may cause the destruction of the friction component if it

is brittle and hard. If, however, it is softer than the base material and is instantaneously renewed after being mechanically destroyed, it weakens the friction and reduces wear during contact of the shaft with the bearing in variable regimes (acceleration on starting, braking before stopping, inertial loads, vibration). Essentially, the gas in this case acts as an active supplier of solid lubricant. Effective gaseous lubricants of this kind are chlorine and hydrogen sulfide.

The greatest antiwear effect is produced by a gas which does not act on the materials of the friction component at ordinary operating temperature, but is adsorbed by the surface, and during frictional heating at the instant of contact decomposes, reacts with the contact surface, and instantaneously restores the worn film. An action of this kind is exhibited, in particular, by halogenated hydrocarbons CF_2Br_2 , CF_3Br , CF_2Cl_2 , and sulfur hexafluoride SF_6 . Atomized oil may be mixed into the gas to provide boundary lubrication of the film, but the thermal stability of the lubricant in this case is limited by the properties of the oil. Cooling of the friction components with a particularly high temperature regime can best be obtained with hydrogen lubrication, since hydrogen has a very high heat capacity and thermal conductivity [37, 59, 70].

CHARACTERISTICS OF LUBRICATION OF TURBOPROP ENGINES AND OILS USED IN THEM

Effect of Reduction Gear

Turboprop airplane engines have a reduction gear which reduces the speed of rotation in the power transmission from the turbine shaft to the propeller by a factor of 10-15, and in helicopter engines, by several tens. There is a corresponding increase of the twisting moment and load in the meshing of the reduction gears. In addition, they operate with a much longer duration of contact than in antifriction bearings. Oil for a TPE reduction gear must be more viscous than oil

for lubricating bearings, with a higher lubricating capacity and better antiwear properties. TPE are characterized by a marked heat transfer into the oil owing to the transformation of the friction power in the reduction gear, corresponding to several tens of horsepower, into heat. Because of the necessity of removing this heat, the amount of oil and its flow rate in TPE is several times as large as in TJE.

The fairly high thermal regime of the bearings, particularly of the turbine, and the heating up of the oil in the reduction gear make it necessary to use oil with a high thermal oxidation stability in TJE. It is difficult to combine with the good lubricating and antiseize properties and petroleum oils. Therefore, the development and introduction of synthetic oils for TJE began earlier than for TPE. The oil properties essential for the operation of TPE reduction gear and possible aftereffects of unsatisfactory oil quality are presented in Fig. 45 on the right [37, 59, 92, 112].

Synthetic oils for TPE

VNII NP-7 synthetic oil (viscosity 7.5-8.0 cS at 100°C) is used in airplane TPE. It consists of the same diester base used in the production of synthetic oils for TJE, and a thickener, i.e., a polymer dissolved in the base. Having a fairly high viscosity, required for lubricating the high load TPE reduction gear, thickened VNII NP-7 oil has a mildly sloping viscosity-temperature characteristic typical of its low viscosity base (Fig. 47). Thus, the chief disadvantage of viscous oils, i.e., a sharp increase in viscosity with decreasing temperature, is removed. This oil provides for starting of the engine, without preheating, approximately down to 0°C. "Grinding" of the viscosity additive during prolonged operation of the oils leads to a certain decrease in oil viscosity.

For helicopter gas-turbine power plants, there is a single synthetic polyester oil B-3V (viscosity no less than 5.0 cS at 100°C), providing for lubrication of the engine and main reduction gear. In viscous properties, it is intermediate between the synthetic oil used in airplane TPE, and oils for TJE (Fig. 47). The lower viscosity of this oil in the main operating temperature range improves its circulation in the zone of lubricated friction components and promotes their efficient cooling.

Both grades of TPE synthetic oils solidify below -60°C. Their antiwear and antiseize properties are due to a surface-active base as well as to an effective additive, tricresyl phosphate or mercaptobenzothiazole, added in larger quantities than to TJE oils. The usual requirements imposed on the antiwear properties of oils for TPE include a critical load on the four-ball tester no smaller than 90 kg, or twice as high as for MS-20 petroleum residual oil (Fig. 40).

The oils are designed for operation without change during the entire service life of the TPE, which is several thousand hours. In order to provide for stability of the oils and reduce their action on the engine parts during such prolonged operation, the composition of synthetic oils for TPE includes an antioxidant and anticorrosive additive. Because of the toxicity of the additives, the same safety measures must be observed as those specified in the case of synthetic oils for TJE [1, 37, 59, 65, 71, 96].

Blends of Petroleum Oils

In addition to synthetic oils, the majority of TPE can use petroleum oil blends of the following three types with limitations on the change period: viscosities in the range of 4.5-6.0 cS, 6-7 cS, and 9-13 cS at 100°C. Previously, they were the main lubricant for TP. In these oil blends, the proposed carrier of the

quality necessary for lubricating the bearings of TPE rotors is a low-viscosity oil (MK-8, MK-6, MS-6 or transformer oil), and the carrier of antiwear properties ensuring normal operation of the reduction gear is a high-viscosity oil obtained from the residual fraction of fuel oil, rich in surface active substances (grades MK-22, MS-20 or MS-20S, designed for aviation piston engines).

The compromise character of the blend of two different oils has certain disadvantages. After the evaporation of light fractions, lacquering on the hot turbine bearings increases, and the starting properties decline. The viscosity-temperature characteristics of a blend with a viscosity of 9-13 cS at 100°C (Fig. 47) are altogether unsatisfactory. Consequently, at an external temperature below 0-5°C, the hot oil in certain types of airplanes must be drained after the flight, and fresh oil must be warmed up and poured into the tanks before starting the engine.

A sufficiently viscous oil satisfactorily operating in TPE at low temperature can be obtained by thickening low-viscosity petroleum oil with a high-molecular polymer (for example, polymethacrylate, polyisobutylene). The required antiwear and other qualities are imparted to it by a set of additives. In view of the scarcity of synthetic oil for airplane TPE, use may be made of thickened petroleum oil of this kind with additives having a viscosity of no less than 7.5 cS at 100°C - MN-7.5 [1, 37, 59].

Foreign Grades

Abroad, lubrication of TPE is done mainly with British synthetic polyester oil Turbooil-750 (its previous brand name was Turbooil-35, and it is sometimes designated 35N), containing a polymethacrylate type thickener. Its viscosity is not less than 7.5 cS at 99°C. It has distinctive antiwear characteristics,

but insufficiently satisfactory starting properties. A synthetic oil of similar viscosity characteristics, consisting of 66% dioctyl sebacate, 28% polyglycol ether and 6% various additives, is produced by the company Castrol Ltd, under the brand names Castrol 98 or OX-38. These oils are used not only in TPE, but also in certain types of TJE. A new synthetic oil, Extra Turbooil-724 named by Esso and characterized by a high thermal oxidation stability, has also been put on the market.

In addition to synthetic oils, petroleum oils of different viscosity are used: British and American grades 1010 or Turbooil-2 (viscosity at 99°C, not less than 2.5 cS), Turbooil-3 (not less than 3.5 cS), Turbooil-9 (in the range 8.7-9.3 cS), grades 1080 and 1100 (in the range 19-21 cS), and the French oil Air-3512.

Both the foreign and the domestic experience and corresponding calculations show that synthetic oils for TPE in comparison with petroleum oils not only provide service advantages and reliability, but are also advantageous in a commercial sense, despite their significantly higher cost. Savings are achieved by using synthetic as a result of an increase in the service life of the oil and decrease in the investment of the time and fuel required to preheat the engines before starting. In addition, spent synthetic oils are easy to regenerate [37, 59].

OILS FOR PISTON ENGINES

Lubrication System

Aircraft piston engines have a complex lubrication system, and the oil operates under heavy-duty conditions. The oil in the engine circulates at a pressure from 4 to 10 atmospheres, most of it being used to lubricate the large

area of high-load sliding friction components, reaching 1 m^2 . Lubrication of the cylinder-piston group is carried out by supplying the oil to the connecting rod small ends and atomizing it; a certain amount of oil inevitably enters the combustion chamber and burns up. In order to achieve liquid friction (formation of an oil wedge) and seal the clearance between the pistons and cylinders to prevent the entry of combustion products into the crankcase, the oil should have a high viscosity under high operating temperature conditions - no less than 20-22 cS at 100°C [11, 59].

Importance of Viscosity

If the viscosity is insufficient, the liquid oil layer cannot be held in the clearances, and consequently, the wear of the parts increases, the sealing of piston rings is adversely affected, the engine compression and power decreases, and leakage of the gases into the crankcase and contamination of the oil take place, resulting in an increased corrosion of the bearings and sludging. The excessively liquid oil is splattered into the cylinders during the motion of the pistons, causing an increase in oil consumption, deposition of carbon increases, the plugs become coated with oil and misfiring takes place during ignition, knocking occurs, and the surface of the piston and other parts of the combustion chamber is attacked.

However, an excessively high oil viscosity is also undesirable, since it leads to an increase in the forces of friction, especially at low temperatures, causing an increase in the power expended in pumping the oil and in friction under normal running conditions. Starting of the engine becomes difficult, the flow rate of the oil through the network of channels of the oil system decreases, splattering of the oil increases, and an oil deficiency takes place: fresh oil

does not reach the friction components, and the oil present in them heats up as a result of friction and flows out. As in the case of too low a viscosity, the result is increased wear or even seizure and galling of the rubbing parts.

Oil for piston engines should have a high lubricating capacity, the boundary film of oils should protect the engine components from dry friction during starting and stopping, and in addition, ensure a reliable operation of the reduction gear and other power transmissions where conditions for the formation of a liquid oil wedge do not exist. This is partly ensured by a high viscosity, which promotes the formation of a thick surface layer of oil, but the oil composition should include surface-active compounds which are carriers of lubricating capacity [1, 59, 72].

Stability Requirements

In connection with the high-temperature conditions in the zone of the piston group (200-300°C) and contact with hot gas and air, conditions for intensive lacquering are created during the operation of an engine. The lacquer, which collects in the piston grooves, may block the piston rings and even jam them, possibly causing breakage of the rings, galling of the cylinder face, and malfunction of the engine. Thus, an extensive purification of oil is necessary to remove unstable organic compounds tending to form lacquers, which decrease the lubricating capacity of the oil. The need for a high purification is also due to the fact that the material of piston engine bearings, lead bronze, is marked by a considerable catalytic action, which enhances the oxidation process in oil, including the formation of corrosive substances. At the same time, lead bronze is unstable to corrosion and extremely sensitive to contamination of the oil [59, 72].

Oil Grades

All aircraft piston engines use the oils MK-22, MS-20, and a very similar oil from sulfur crudes, MS-20S (in these oil brands, the number denotes the lower viscosity limit at 100°C). These are comparatively expensive and scarce residual oils with a high degree of purification, obtained from select oil crudes. The residual products of vacuum distillation of fuel oil contain more polar substances, which are carriers of lubricating capacity, than distillate products do. The least stable are removed during oil refining. Thus, the conflict between the incompatible requirements of a good lubricating capacity and thermal stability is resolved to some extent.

Experiment has shown that all three grades of oil are practically equivalent in operation in engines. In view of this fact, they can be mixed in any proportions during refueling of airplanes. The differences in physicochemical properties which exist between these oils (in solidification temperature, acid number, coking capacity, etc.) are important only from the standpoint of quality control of fresh oil of each brand. They are practically equalized in the course of operation in the engine. Sulfur, which is present in MS-20S oil in amounts up to 1%, enters into the composition of inactive compounds and has no adverse influence on engines (1, 65).

Starting Properties

All three oil grades have satisfactory low-temperature properties: MS-20 and MS-20S oils solidify at -18°C, and MK-22, at -14°C. Solidification takes place as a result of a sharp increase in viscosity with decreasing temperature (see Fig. 47), and for this reason, depressants cannot lower the solidification point.

In the winter, to facilitate the next starting of an aircraft piston engine, the oil is diluted with gasoline (added in the amount of 10% of the capacity of the oil system) before the engine is turned off. As a result of the dilution, the solidification temperature of the oil is lowered by approximately 10°C , and starting of the engine thus becomes possible down to a temperature of minus $25-30^{\circ}\text{C}$ (with undiluted oil, down to minus $5-10^{\circ}$). The dilution enables the mobile liquid lubricant to reach all the rubbing parts and facilitates the rotation of the engine shaft by the starter. After the engine is started, gasoline evaporates from the diluted oil, and the high viscosity of the oil is gradually restored. Only 2-3% of gasoline remains in the oil; such an amount of fuel in the oil is present even without artificial dilution, as a result of penetration of the fuel from the engine cylinders.

At a temperature below minus $25-30^{\circ}\text{C}$, the oil is drained from the oil system after the flights, and before starting is heated to $90-100^{\circ}\text{C}$, and the system is refilled. Before pouring the hot oil into the oil system, the engine is warmed up by means of airport equipment [1, 65, 81].

Service Life

The properties of fresh oil during the first hours of its operation in an engine change sharply. Because of accumulation of oxidation and decomposition products, the acid number and coking capacity increase rapidly. Mechanical impurities, i.e., dust and wear particles, appear in the oil. Along with the lead oxides coming from the fuel, they cause an increased ash content. The viscosity and other indices also change. Subsequently, these changes become less pronounced (see Fig. 44a) as a result of addition of oil or stabilization of the oil operating in the engine. The stabilization is promoted by filtration of the oil, its

centrifuging inside the crankshaft of the engine, and also by the formation, during oxidation of the oil, of phenolic compounds which inhibit further oxidation.

Oils with physicochemical indices obtained after their stabilization after several tens of hours of operation of the oil in the engine (with a coking capacity, ash content, etc. that have increased many times over) fully ensure its normal operation. Therefore, a frequent oil change is not necessary. In most aircraft piston engines, the oil is replaced every 100 hours of operating time [1, 59, 72, 81].

Foreign Grades

Many foreign petroleum oils for aircraft piston engines have properties similar to domestic oils, in particular, American oils of grades 1065, 1080 and 1100, and the British brand Oil-100 or B/O (international designation OM-270), corresponding to the American brand 1100. In addition, a more viscous oil for tropical conditions is used (viscosity in the range of 25-28 cS at 99°C under brand Oil-120 or grade C (International designation OM-370) [59, 72].

CHAPTER 9

OILS FOR MECHANISMS AND EQUIPMENT OF FLYING VEHICLES TRANSMISSION OILS

Operational Characteristics

Particularly high contact loads characterize the reduction gears of the tail rotor transmission and hinges of the automatic pitch-control mechanism of the main rotor of helicopters, as well as the worm mechanisms of the steering gear of airplanes. The conditions of operation of the oil in these mechanisms are different than in the engine. At any given moment, the oil operates only on a narrow portion of the contact in the form of a thin boundary film adsorbed on the surface. Because of the very large load, the liquid layer of oil in the contact zone of the power transmission is excluded. However, even the boundary film on the heaviest-loaded sections is partially destroyed.

In order that the transmission oil protect the gears, worm couples and hinges from wear, galling and welding (seizing), it should first have a very high lubricating capacity - adhere to the friction surfaces better than any other oils, and second, have very high antiseize properties. Essentially, they consist in a chemical action of the oil on the metal, as a result of which the surface layer itself of the parts in the contact zone changes into a solid lubricating (oxide, sulfide, phosphide, chloride, etc.) film. Since this solid film is also destroyed in the course of friction under a high contact pressure, the chemical action of the oil on the metal should be so intense as to cause its immediate restoration, i.e., it must not allow the metal to be bared.

The oil temperature outside the contact zone is usually moderate (of the order of 50-60°C); the area of contact between the oil and atmospheric oxygen is small. Therefore, conditions do not arise for any intensive processes of oxidation or decomposition in the volume of the oil or its corrosive action on the parts outside the contact zone. Hence, there is no need to impose on transmission oils the requirement of stability at high temperatures and absence of corrosive impurities [11, 59].

Composition of Oils

As we know, the carriers of lubricating capacity of petroleum oil are resins unstable at high temperatures, corrosive organic acids, and sulfur and certain other compounds present therein. Because these substances are dangerous for engines at high temperatures, it is necessary essentially to remove them from the oil. However, under operating conditions characteristic of transmission oils, their presence is entirely permissible. Therefore, transmission oils are made by using unpurified petroleum oils and a resinous extract obtained from motor oils during their selective treatment. Another way of providing for the necessary lubricating capacity is to prepare transmission oils from a synthetic base which has this capacity in the first place.

To ensure antiseize properties, in addition to natural chemically active substances, the composition of transmission oils is made to include additives containing chlorine, phosphorus, and sulfur, which form with the surface layer of the metal an easily destroyed corrosion film that sharply decreases the coefficient of friction. It is best to include these additives in the composition of compounds which have practically no effect on the metal at the ordinary temperature of the oil in the volume of the housing of the mechanism

(i.e., below 100°C), while in the contact zone, as the temperature rises to 150-200°C and above as a result of friction, they decompose and react with the metal.

The fusion temperature of corrosion films (particularly phosphide ones) is lower than that of the metal. The fusion of a thin layer of heavily loaded rubbing surfaces during heating caused by friction promotes their mutual smoothing out and running in. A smooth surface in turn better holds the boundary oil film protecting the metal from wear. As we know, on melting, the corrosion surface layer does not cause seizure of the metals, thus preventing welding and breakage of teeth, hinges, etc. [41, 72].

Contradictory Viscosity Requirements

For many years, only high-viscosity oils were used for lubricating transmissions. They unquestionably have better antiwear properties than similar low- and medium-viscosity oils containing no antiwear additives, since the boundary lubricating film is thicker the higher the viscosity. However, the antiwear qualities of an oil can be secured independently of the viscosity by using additives. In this case it is desirable that the oil have a moderate viscosity that does not interfere with the start of motion of the transmission at low temperatures. Under normal operating conditions, a more mobile low-viscosity oil provides for a better heat transfer from gears and other friction pairs, promoting an improvement of their boundary lubrication [40, 41, 72].

Oil Grades

At the present time, hypoid oil, i.e., a sulfurized mixture of the resinous extract of motor oils and low-viscosity oil distillate with an admixture of

depressant, is used for the lubrication of the intermediate and tail reduction gears of helicopters (and for the MI-1 and main reduction gear). Hypoid oil contains 1.5-3.5% sulfur, including free sulfur. It effectively prevents galling and seizure of the metal at high loads, but the wear associated with its use is significant. This wear is due to its high viscosity (20-30 cS at 100°C). The motion of the oil inside the reduction gear housing is insufficient, the gears are inadequately cooled, and the lubricating boundary film is not very stable. In addition, viscous hypoid oil has unsatisfactory low-temperature properties - the solidification point of summer oil is around -5°C, and that of winter oil, -20°C. In winter, the hypoid oil of helicopters is diluted with low-viscosity low-freezing AMG-10 hydrooil in the proportion of 2:1.

A mixture of hypoid oil with AMG-10 hydraulic oil is also used in certain types of airplanes in the worm gear mechanisms of the stabilizer adjustment. Similar to transmission oils in composition and properties is the liquid grease TsIATIM-208, used in the hydraulic drive and landing-gear retraction mechanisms of heavy airplanes.

The hinges of the automatic pitch-control mechanisms of helicopters are lubricated with MS-20 oil at positive temperatures, and at subzero temperatures in regions of moderate frost, with MS-14 oil, which differs from MS-20 in a lower viscosity and lower freezing temperature (not above -30°C). The possibility of using these oils, which are obtained from the residual heavy oil fraction, as transmission oils, is due to their significant content of surface-active substances. At low temperatures in cold regions, special hinge oil VNII NP-25, useful in the range from -50°C to +40°C, is employed. It is a mixture, having a comparatively low viscosity (for a given class of oils), of diester and petroleum oil with antiseize and antioxidant additives. Its viscosity at 100°C is not less than 9.8 cS,

at -40°C not more than 55000 cS, and its solidification temperature is not above -54°C . It is superior to MS-20 oil in antiseize properties [65, 96].

OILS FOR MODERATELY LOADED MECHNISMS DEVICES AND COMPONENTS

Petroleum Oils

In airplanes and helicopters, the lubrication of various mechnisms, devices and components operating at moderate specific pressures involves the use of engine oils and special grades of petroleum and synthetic oils, as well as vegetable and animal fats.

AU spindle oil is used inlanding gear joints and certain armanent components. It is a highly refined petroleum oil with a low solidification temperature (not above -45°C), slightly more viscous than TJE oils (its visocity is 12-14 cS at 50°C).

MVS oil is used for lubricating piston rod cups and cylinder seals in the actuating mechanisms of air systems. This is a typical thickened oil prepared in much the same way as AMG-10 hydraulic oil. Its base is a high-boiling, low-freezing kerosene fraction, and the thickener is Vinypol, added in large quantity, up to 25%. This provides a combination of high viscosity (70-90 cS at 50°C) and desirable low-temperature properties (a freezing temperature not above -60°C). MVS oil makes the seals elastic, and ensures a reliable and smooth operation of the devices controlled by compressed air. The stability of MVS oil is provided by an antioxidant additive, α -naphthylamine (0.1%). The color of MVS oil is red or pink [65, 72, 96].

Organosilicon Oil

Lubrication of rubber parts rubbing against a metal in air systems also involves the use of lubricant No. 6, a high-viscosity polysiloxane liquid (200-275 cS at 20°C), colorless or light yellow. Only an organosilicon oil can have desirable low-temperature properties at such a viscosity; lubricant No. 6 has a solidification temperature below -70°C, and at -60°C has a much lower viscosity than petroleum and synthetic engine oils (not more than 15,000 cS). For all practical purposes it does not evaporate during service. While wetting the rubber, the lubricant does not attack it. It does not form a lubricating boundary film on steel [72].

Natural Fats

In helicopters, the rubber rings of the tail rotor mounts are lubricated with vegetable castor oil. Its viscosity is around 130 cS at 50°C, and its solidification point is -16°C; the vaporizability of the oil is insignificant. It is characterized by an unusually strong adhesiveness. The leather locks of helicopter rotor blades are lubricated with fish fat, extracted with solvents during fish processing. It is a mixture of various triglycerides of unsaturated organic acids. By softening leather seals, it provides for their tight adhesion [59].

INSTRUMENT OILS

Operating Conditions

Instrument oils are used for decreasing the friction and wear and simultaneously protecting from corrosion various components of electronic and sighting equipment,

high-speed gyroscopic instruments and tachometers, electric machines, cooling turbines, photographic equipment, clock mechanisms, pointer instruments in cabins, etc. They operate over a wide temperature range, from -60°C to $+100^{\circ}\text{C}$ and higher. The rubbing components of the instruments usually are not subjected to any considerable or lasting loads and do not undergo vibrations. The speed of the parts in certain instruments is very high (for example, the speed of rotation of a gyroscope rotor is 15,000-30,000 rpm). The displacement of instrument parts (in particular, the start of a displacement) should never be braked with an oil, since this might cause errors in readings and signals. For this reason, instrument oils should have a low viscosity (also at low temperatures) that provides for free displacement of the rubbing parts of the instruments but is sufficient to prevent oil leakage. In the absence of oil containers, of great importance is a high surface tension of the oil, which prevents its spreading. Instrument oil should possess a lubricating capacity in relation to all the special materials used in the instruments, i.e., rare and precious metals, solid minerals, and glass. It must be very pure and chemically passive toward the materials of the instruments. Many instruments are lubricated only during their manufacture and repair; their lubrication during service is excluded so as to avoid misadjustments and the introduction of contaminants. Because of the long service life of instrument oils, it is necessary that they be chemically very stable at normal temperature and that they do not evaporate [59, 81].

Organosilicon Oils

The most important group of instrument oils are OKB-122 oils, whose main component is ethylpolysiloxane liquid. It has a record mildly sloping viscosity-temperature characteristic, is stable and involatile, but does not possess a

sufficient lubricating capacity. To improve its lubricating properties, petroleum oils - AU spindle oil or MS-14 - are added to it (in the amount of 15 to 40%). The solidification point of OKB-122 oils is -70°C . They are stable to oxidation. The flash point of these oils (which characterizes their vaporizability) is high, of the order of $160-170^{\circ}\text{C}$. The lowest viscosity of this group of oils is displayed by grades OKB-122-3 and OKB-122-4 (from 11 to 14 cS at 50°C), a higher viscosity is displayed by OKB-122-5 and OKB-122-14 (of the order of 20 cS at 50°C), and the highest, by OKB-122-16 (about 25 cS at 50°C). Organosilicon oils can react with copper and lead, and they are therefore incompatible with brass and unsuitable for certain devices and instruments with important brass parts [59, 70, 71, 96].

MVP Instrument Oil

Among natural petroleum oil distillates with a viscosity of about 6 cS at 50°C , MVP oil is characterized by the lowest solidification temperature (below -60°C). In order to reach such a solidification temperature, this oil is prepared from paraffin-free petroleum. Nevertheless, MVP oil at approximately -40° is already practically useless because of the increase in viscosity. Owing to a very high refining, MVP oil does not cause metal corrosion even in prolonged service, but is not characterized by a desirable lubricating capacity, since its refining removes substances which are carriers of this property [59, 65].

Clockwork Oils

Clockwork mechanisms and certain components of electronic equipment of aircraft are lubricated with bone oil (obtained from hoof fat) and MTs-3 clockwork oil, consisting of a mixture of bone oil and low-viscosity petroleum oil containing

an antioxidant additive. Bone oil is characterized by its capacity to be held in miniature friction components without spreading or evaporating (flash point above 300°C). It has a low friction coefficient of the boundary layer. All this makes it irreplaceable for clockwork mechanisms. The viscosity of bone oil is 80-95 cS at 20°C, and its solidification point is -18°C (this is important only from the standpoint of the possibility of its introduction into the mechanism). The viscosity and solidification temperature of MTs-3 oil are somewhat lower [81, 96].

CHAPTER 10

GREASES

COMPOSITION AND STRUCTURE OF GREASES

General Characteristics

Greases are microheterogeneous mixtures of liquid oils with solid thickeners, which limit their fluidity. The majority of greases are plastic (plasticity is the ability of solids acted on by external forces to change their shape without being damaged). Plastic lubricants are intermediate between solids and liquids: they do not spread under the influence of their own weight or ordinary inertial forces, and under high loads flow as viscous liquids do. This gives them special service characteristics and permits their use in friction components where a liquid lubricant is not retained or where its penetration is difficult. They are also used for sealing rubber and other compounds in pipelines, rivet joints, etc., for protecting open surfaces of parts from contamination and corrosion, and finally, for technological purposes, in particular, for fitting and facilitating the running in of rubbing parts. In addition to plastic lubricants, there are also liquid and semiliquid (pastelike) greases which flow under their own weight. They are frequently more convenient than plastic lubricants for lubricating and cleaning barrel weapons, for internal conservation of engines, and in technological processes.

According to their applications, greases are usually divided into four groups: antifriction, sealing, protective (or preservation) and technological. However, the applications of greases often overlap. This applies particularly to antifriction

greases. As a rule, they simultaneously protect from corrosion, seal friction components in order to protect them from contaminants, and promote a useful modification of rubbing surfaces (fitting in) [17, 59, 64, 65].

Thickeners

The thickeners usually employed in the composition of lubricants are solid, but fairly plastic substances, mainly soaps (sodium, lithium, calcium, etc.) and solid hydrocarbons (paraffin, ceresin). Certain lubricants are thickened with specially treated silica gel, organic and fluorocarbon polymers, and solid lubricants such as graphite and molybdenum disulfide. The thickener is present in the lubricants in small amounts (usually, not more than 10-20% of the weight of the lubricant).

In plastic lubricants, the intergrown crystals of thickener form a continuous but loose structural framework of lubricant whose cells contain a liquid oil. The structure of the skeleton of semiliquid lubricants is also continuous, but the bonds between neighboring thickener crystals are so weak that even when they are acted upon by slight forces (including the forces of gravity), they acquire a sporadic character: they break, then are restored. In liquid lubricants, solid particles of the thickener are suspended in oil; they give rise to a thick consistency, inhibiting the flow of the liquid phase.

Usually, the crystals of the thickener are in the shape of filaments or ribbons (Fig. 50). Their significant length on the scale of microinhomogeneous systems (from hundredths of tenths of a millimeter) gives a microfibrinous structure to the three-dimensional lubricant network formed by them. The transverse dimensions

of the crystals are of the order of one tenth of a micron, producing an enormous contact area between the two phases that is typical of colloidal systems, and over which the adsorption forces are acting. This imparts stability and inseparability, so-called colloidal stability, to the two-phase system.



Fig. 50. Microstructure of TsiATIM-210 lubricant ($\times 10,000$); a. - prior to mechanical action; b. - following a strong mechanical action (400 strokes per minute for 2 hours)

The properties of plastic lubricants are chiefly determined by the thickener, and to a lesser extent by the oil. Thus, sodium soap imparts strength and infusibility to a lubricant, but dissolves in water, so that sodium lubricants soften in a moist medium. Lithium soap is almost as infusible as sodium soap, but less soluble in water. A high moisture resistance is displayed by lubricants prepared from calcium soap, whose structural framework is stabilized by water; however, they are inefficient at temperatures above $80-100^{\circ}\text{C}$: owing to the loss of water, the soap framework breaks down, and the oil separates from it. The highest moisture resistance is imparted to the lubricant by solid hydrocarbon thickeners (paraffin, ceresin), but they melt at a low temperature [59, 72].

Effect of Oil

Certain properties of greases depend on the oil they contain. Thus, cold resistance or the lower temperature limit of the usefulness of greases depends on how low are the viscosity and solidification temperature of the oil. However, greases containing low-viscosity oils do not tolerate loads as well (they eliminate the oil under load). Because of the vaporizability and insufficient chemical stability of petroleum oils, greases containing them are unsuitable for prolonged operation at high temperatures, in corrosive media, or in vacuum. The nature of the oil entering into the composition of the grease determines the strength of the boundary film on the friction surface; the best oil in these respects is vegetable castor oil.

In addition to oils and thickeners, the composition of certain grades of greases includes additives, i.e., antioxidant, structure-stabilizing, antiwear, and corrosion-inhibiting additives [59, 72].

STRUCTURAL-MECHANICAL PROPERTIES OF PLASTIC GREASES

Differences from Solids and Liquids

The peculiarity of the disperse structure of plastic greases gives them special mechanical properties differing from those of solids and liquids. Thus in contrast to solids, the strength of a plastic grease depends to a large extent on the temperature and time of "rest" following the preceding load, and the viscosity depends on the rate of flow, in contrast to normal liquids. This is due to the fact that under the influence of external forces, bonds are broken in the lubricant, and deformation of the thickener crystals takes place (see in Fig. 50 the electron photomicrographs of a grease before and after a mechanical action).

The restoration of the broken bonds and of the initial structure of the framework takes place only after a certain time has elapsed [17, 59].

Ultimate Strength

Under light loads, the grease retains its internal structure and is deformed elastically like a solid (straight line on the left in Fig. 51). As the load increases, the structural framework of the grease begins to break down, and the grease gradually loses the properties of a solid and begins to flow like a viscous liquid. The maximum shearing stress corresponding to this transition is known as the ultimate strength or yield point of the grease. In the ordinary range of working temperatures, it amounts to one to several grams per square centimeter, i.e., is millions of times lower than for structural materials. On the yield point of the grease depends the magnitude of the initial shearing force (for example, the shearing force of the start of rotation of an anti-friction bearing), and also its ability to be retained in the component being lubricated while being acted upon by inertial forces. Thus, it has been experimentally established that greases are thrown from the antifriction bearing by centrifugal forces when a shearing stress is reached that is equal to one-fourth of the ultimate strength (the shearing stress is proportional to the square of the number of revolutions).

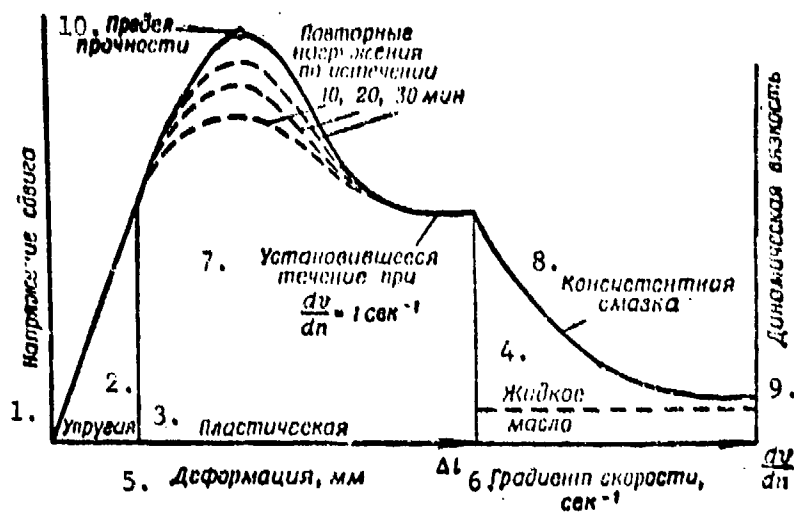


Fig. 51. Diagram for determining the specific mechanical properties of greases. Key:

1. Shearing stress; 2. Elastic; 3. Plastic;
4. Liquid oil; 5. Deformation, mm; 6. Velocity gradient, sec^{-1} ;
8. Grease; 9. Dynamic viscosity;
10. Ultimate strength; 11. Repeated loadings after 10-20, 30 min.

In repeated loadings, before the restoration of broken bonds, the ultimate strength turns out to be lower than in the first loading, but as the "rest" time increases, it approaches the initial value (dashed lines on the left in Fig. 51). A periodic turning of the bearings which have seized at low temperatures can reduce the initial shearing force or prevent shearing of the grease. The ultimate strength depends on the nature and amount of thickener in the grease, and depends little on the oil viscosity. The ultimate strength is measured with a plastometer (Fig. 52), in which the shearing stress is increased by means of a press utilizing the force effect of thermal expansion of the oil. The ultimate strength (yield point) of the lubricant corresponds to the maximum of the manometer readings [64].

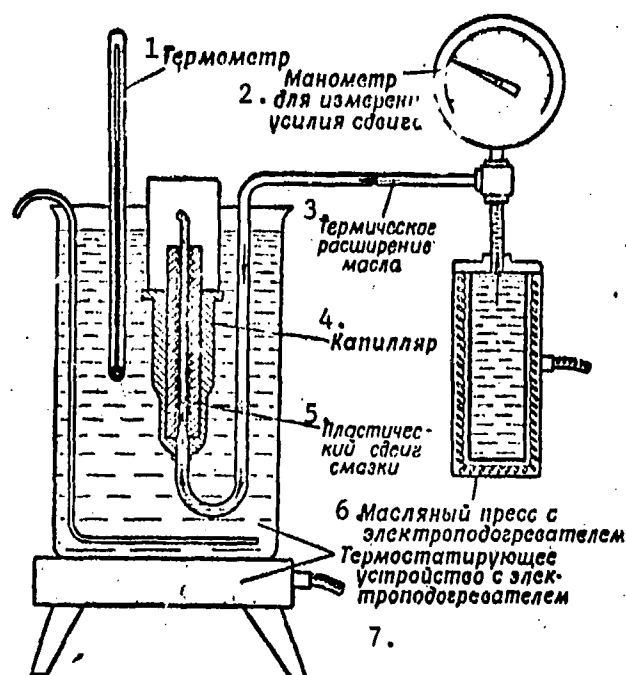


Fig. 52. Diagram of plastometer for measuring the ultimate strength of a grease. Key:

1. Thermometer; 2. Manometer for measuring the shearing strength; 3. Thermal expansion of oil;
4. Capillary; 5. Plastic displacement of grease;
6. Oil press with electric heater; 7. Thermostat with electric heater.

Viscosity

When a grease is acted upon by forces exceeding its shearing strength, the grease flows, and its properties are characterized by viscosity. At the same time, the magnitude of the viscosity reflects not only the internal friction between layers moving over one another, but also the instantaneous equilibrium between the processes of destruction and restoration of the framework of the lubricant, equilibrium which also depends on the rate of relative displacement of the lubricant layers. Therefore, the viscosity of plastic greases decreases with rising shearing velocity gradient $\frac{dv}{dn}$, a more extensive breakdown of the structural framework of the grease takes place, the bonds between the

thickener particles are destroyed almost completely, and the grease becomes similar to a thickened oil.

The viscosity-temperature characteristic of greases has a very mild slope; as the temperature drops, the viscosity increases hundreds and thousands of times more slowly than the viscosities of the oils entering into its composition. This is due to the fact that the flow resistance of the grease is chiefly due to the cohesion of the thickener particles, which is considerably less dependent on temperature than the viscosity of the initial oil.

The viscous properties of greases determine the friction loss in the friction bearings where they are used, starting rates at low temperatures, and the possibility of delivering the greases to the friction components along channels (grease lines). Practical viscosity standards are established on the basis of the upper limit at subzero temperatures. The tests are carried out on an automatic viscometer in which the grease is pressed out of a capillary by a spring piston at a variable rate. The best viscous properties are displayed by greases consisting of a low-viscosity oil and a large amount of thickener. They retain a low viscosity at low temperatures and their viscosity decreases sharply with increasing sliding velocity. As a result, the force of friction undergoes little change when the operating conditions change significantly [64].

Penetration

The consistency of plastic greases which to some extent reflects their structural-mechanical properties is checked by determining penetration, i.e., the depth (in tenths of a millimeter) of immersion of the cone of a penetrometer (Fig. 53) into the grease in 5 sec under a load of 150 g. The softer the grease,

the higher the penetration number. Plastic greases for aviation technology have a penetration from 170 to 360 at 20°C [64].

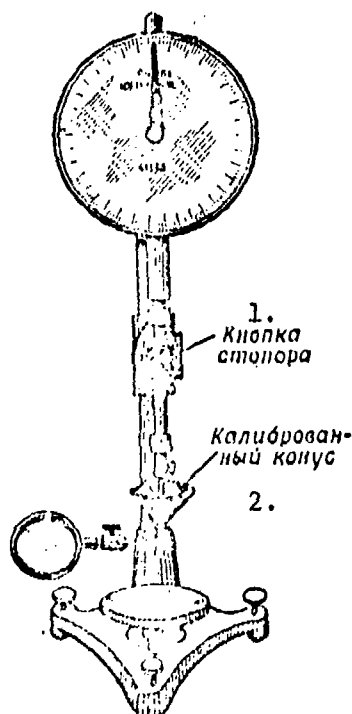


Fig. 53. Penetrometer
Key:

1. Knob of stopper;
2. Calibrated cone.

Thermal Stability

Another structural-mechanical property of plastic greases from the standpoint of their physical nature is thermal stability. The ultimate strength of a grease decreases to zero with rising temperature, and the grease acquires the ability to flow under very weak forces, including the action of their own weight. This is explained by an increase in the kinetic energy of the thickener particles (mainly an increase in vibrational thermal motion), resulting in the rupture of the bonds between them and destruction of the framework. It is true

that the framework of hydrocarbon greases breaks down even earlier as a result of melting of the thickener, and that the calcium greases, as a result of loss of the water stabilizing the framework.

The thermal stability of greases is controlled by means of the dropping point, i.e., the temperature at which the first drop falls from a grease heated in a special device (Fig. 54). Plastic greases are used at temperatures no lower than 10-20°C under their dropping point in order to avoid leakage of the grease from the friction component. Greases with a dropping point above 100°C are considered high-melting, from 65 to 100°C, medium-melting, and below 65°C, low melting. In the brands of certain greases, the thermal stability is indicated by the letter T, S, or N, respectively, which is in second place.

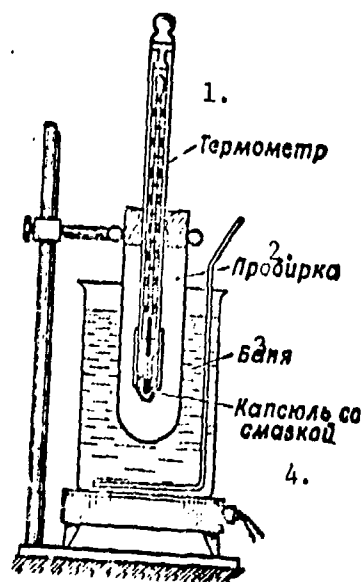


Fig. 54. Instrument for determining the dropping point of greases. Key:

1. Thermometer; 2. Test tube; 3. Bath;
4. Capsule containing grease.

Greases with the highest thermal stability have no dropping point. Their thickener, silica gel, molybdenum disulfide, graphite, or carbon black, ground to colloidal particle size, does not melt to very high temperatures. The very small size of its particles ensures the predominance of surface bonding forces over the loosening effect of thermal agitation. The upper temperature limit of

applicability of such greases is determined by the properties of the oil included in their composition [59, 64, 72].

STABILITY AND PROTECTIVE PROPERTIES OF GREASES

Basic Concepts

The period of reliable operation of greases in friction components, in joints sealed by the greases, and in the preservation of parts, depends on the stability and protective properties of the greases. The stability of a grease is considered to be its ability to retain its structure and decomposition, and the protective properties consist in its ability to protect the surfaces on which it is deposited from corrosive agents. The indices of stability and protective properties are the changes taking place in the grease or in the materials protected by it during the action of various physical and chemical factors: loads, heating and cooling, vacuum, water and its vapor, oxygen and other chemically reactive substances, dust, radiation, etc. [17, 59].

Physical Stability

The colloidal stability is estimated from the separation of liquid oil in % of the weight of the grease, which is kept under a press for 30 min. The oil which is squeezed out is absorbed into a stack of paper filters (which are weighted before and after the test). Determination of syneresis (the name given to the phenomenon of layer separation in colloidal systems) is carried out during free flow of the oil in the course of a day through the paper filter from a funnel containing the grease, following a vigorous stirring of the grease at 50 or 70°C. When a grease of low colloidal stability is stored in a large container, a significant amount of oil may be squeezed out of the lower layers; a part of the grease turns out to be unsuitable. When used under loads, such greases lose their oil and become enriched with the thickener and thus useless.

The vaporizability of the liquid phase of greases also raises the thickener concentration (up to and including loss of plasticity of the grease, formation of a crust, and cracking of its surface). The vaporizability of greases is quantitatively expressed in percent of weight loss of the grease in an evaporator in 1 hour at 120°C. The worst from this standpoint are greases containing low-viscosity petroleum oil. The vaporizability of the greases increases at low atmospheric pressure under high-altitude conditions and during air cooling [17, 59].

Chemical Stability

Oxidation with atmospheric oxygen affects chiefly the liquid phase of a grease, i.e., the oil. The thickener plays a dual role in this case; it

inhibits the diffusion of oxygen, but the metal cations of the soap thickener are oxidation catalysts. The chemical stability of the grease is estimated from forced oxidation of the grease at an elevated temperature (and for certain greases, at an elevated pressure as well), from the increase in the acid number (or decrease of alkalinity), and also from the magnitude of the pressure decrease, which reflects the amount of added oxygen.

The thermal stability of greases as a characteristic of their efficiency has meaning when applied to greases which become unsuitable on heating below the dropping point or have no dropping point at all. Soap thickeners prepared from inadequately purified synthetic fatty acids cause thermal hardening (gelatinization) of the grease, i.e., its transformation into an elastic solid which may cause failure of antifriction bearings. The oxidation of inorganic thickeners - graphite at 500°C, molybdenum disulfide at 425°C - causes decomposition of the grease [58, 59, 64].

Radiation Resistance

In ordinary greases, the initial stage of irradiation (total dose of the order of $1 \times 10^8 - 2 \times 10^8$ rad) leads to degradation of the thickener, destruction of the framework, and softening or even liquefaction and running of the grease. High irradiation doses (of the order of $10^9 - 10^{10}$ rad) initiate a vigorous oxidation and polymerization of the liquid phase; as a result, aviation greases containing petroleum or polysiloxane oils are converted into a brittle, solid mass. The metals present in soap greases (mainly sodium) acquire induced radioactivity on irradiation [17, 32].

Protective Action

The ability of a grease to protect the surface of a material from atmospheric and other destructive agents is due to its insulating as well as to its active effect. It depends on the stability characteristics discussed above and also on the moisture resistance and impermeability of the grease to water, the absence of mechanical impurities and corrosive substances, and the presence of neutralizing substances and corrosion inhibitors.

On contact with water, mechanical impurities give rise to electrochemical corrosion; metallic particles may play the role of catalyst in the oxidation of the grease itself. In an antifriction grease, abrasive particles capable of scouring the parts are completely inadmissible, since the grease is not filtered during its use. External access of dust attacks soap greases: dust adsorbs and absorbs the oil, and the grease layer dries out and peels off. Mechanical impurities in a grease are easily detectable to the touch, i.e., by rubbing it between one's fingers. Their quantity is determined by dissolving and filtering the grease [17, 53, 72].

Anticorrosive Action

Typical of greases is a slight excess of free alkali: it neutralizes the corrosive acidic products formed during prolonged storage. Some greases inhibit electrochemical corrosion by forming on the metal surface inhibitors which polarize (insulate) the cathodic or anodic portions of galvanic microcells. Finally, the anticorrosive effect of greases may be due to inhibitors forming an

ordinary protective corrosion film. When properly selected, greases can provide better protection of materials from corrosion than paints and other means of protection [59].

Creeping

The adhesion of greases to metal surfaces is usually stronger than the internal bonding between the grease particles. On the other hand, the internal bonds are sufficient to prevent a homogeneous grease from flowing under the influence of its own weight up to a certain temperature. Running of greases from vertical surfaces may occur at a temperature approximately 20°C below the dropping point. This is due to wall syneresis, i.e., an increase in the concentration of liquid oil in the ultrathin layer of grease at the wall. Under the influence of the weight of the grease and adsorption forces of the surface, deformations of the grease framework arise near the wall, microcavities increase, and microcracks appear. They become filled with liquid oil, along the layer of which creeps down the layer of plastic grease adhering to the outside. The creeping temperature should be considered in selecting protective greases for hot climatic conditions, and also when placing parts and materials in long-term storage in warehouses. The grease must not be applied in too thick a layer [17].

ANTIFRICTION GREASES

TsIATIM-201 Grease

Antifriction greases are used to decrease the friction and wear in aircraft and engine control units, landing gear attachments and retraction mechanisms, bearings of wheels and various generating sets, mechanisms of armament, special equipment, and instruments. From the standpoint of convenience of servicing, the same universal grade of grease efficient over a wide range of service conditions is used as often as possible, namely, TsIATIM-201 grease. This grease is the product of thickening of MVP low-viscosity oil with moisture-resistant heat-stable lithium soap (lithium stearate), and contains an antioxidant and simultaneously stabilizing additive, diphenylamine (0.3%). The color of the grease is usually yellow. Its ultimate strength at 50°C should be no less than 2.5 g/cm². The dropping point of this grease is not below 170°C, the practical range of working temperatures is -60°C + 140°C, and in prolonged service, up to +90°C.

Because of the low viscosity of the oil entering into its composition, TsIATIM-201 grease tends toward syneresis, i.e., separation of liquid oil, at a high temperature. It should be stored in a cool place in a shallow container so as to prevent the oil from being squeezed out under the pressure of the higher layers of grease (the usual weight of a package is 850 g). MVP oil evaporates from a thin layer of grease (especially on open surfaces), the grease "dries," and the remaining mass of lithium soap cannot provide for normal operation of the friction components; this makes it unsuitable for prolonged service at temperatures above 90°C. The protective properties of the grease are not pronounced, i.e., the grease is permeable to moisture.

In friction components where the temperature conditions or the specific pressure is higher than what TsiATIM-201 grease can tolerate, grease grades with a higher thermal stability or an improved strength of the boundary film are used. Greases of improved stability are used for instruments and special equipment [59, 65, 72].

NK-50 Grease

In airplane wheel bearings, where the temperature of a landing run reaches 160-180°C, and in the valve mechanisms of piston engines, use is made of NK-50 grease with a dropping point not below 200°C. It is also used as an agent against work hardening and scorching in heavily loaded and heated splined and threaded joints. NK-50 grease is thick and black in color with a greenish shade. It consists of viscous aviation oil MK-22, sodium soap (not moisture-resistant), but even more heat-resistant than lithium soap), and 0.5% of colloidal, very finely divided graphite. The graphite flakes give a high strength to the lubricating film and protect from dry friction of metal against metal at high loads and high temperature. A normal state of the components lubricated by it is obtained for brief periods (up to several hours) at a temperature as high as 400°C.

NK-50 grease has important disadvantages: at a high humidity, it swells, softens, and creeps off the parts, and at low temperatures, solidifies and splits off. For this reason, it is necessary systematically to check friction components operating on NK-50 grease, and if necessary, replenish or replace it. In winter, at temperatures below -25°C, instead of pure NK-50 grease, use is made in airplane wheel bearings of the more cold-resistant mixture of NK-50 and TSIAMTIM-201 greases in the proportion of 3:1 (this composition has the

lowest ultimate strength, lower than pure TsIATIM-201). Before mixing, it is permitted to heat the greases to a temperature no higher than +60°C. NK-50 grease and its mixture with TsIATIM-201 grease is stored in sealed containers in a dry place; the water content of the grease must not exceed 0.3% [59, 65, 72].

Thermally Stable Greases

For friction components located in the hot zone near engines, the most suitable grease is TsIATIM-221 (externally, it resembles TsIATIM-201, but is softer). It is obtained by thickening ethylpolysiloxane liquid, which withstands a temperature up to 300°C, with a composite calcium soap, calcium stearate-acetate (calcium acetate gives stability to calcium soap at high temperatures). The ultimate strength of this load at 50°C is not less than 1.2 g/cm², and the dropping point is above 200°C. Under conditions of still higher temperatures and contact with hot gases, use may be made of PFMS-4s grease of dark color, the product of thickening of polyphenylmethysiloxane liquid, which is very stable to oxidation, with graphite and a pigment thickener. Vaporization of the liquid above 400°C does not cause failure of mechanisms having no high-speed friction components, as the thickener continues to fulfill lubricating functions in these components approximately up to 500°C [59, 65, 70, 72, 96].

Antiwear Greases

Grease 1-13 of yellow or brown color is used for bearings of hinged blades of a variable-pitch propeller subjected to high specific pressures.

It consists of a medium-viscosity petroleum oil thickened with calcium-sodium soap prepared from castor oil. Such soap is characterized by strong adhesion to metal. The dropping point of the grease is not below 120°C, and the maximum operating temperature is 100-110°C. At low temperatures, the grease is useful down to approximately -40°C. Because of the presence of sodium soap, it is inferior to lithium and pure calcium greases in moisture resistance.

TsIATIM-203 grease, of dark-brown color, is designed for helicopter rotor mounts, where the specific pressure is still higher. This grease not only has a high resistance of the boundary lubricating film, but also a chemical activity which protects the metal from galling. It is prepared from transformer oil pre-thickened with Vinpol. The thickener of the grease itself is lithium soap more viscous than in TsIATIM-201 grease, and prepared from sulfurized spermaceti and sulfurized naphthenic acids. The dropping point of TsIATIM-203 grease is not below 150°C. In addition to sulfur (which should be present in amounts not less than 0.2%), the antiseize properties of the grease are provided by an admixture of triphenyl phosphate (0.5%). In colloidal stability, TsIATIM-203 grease is better than TsIATIM-201 because of a lesser mobility of the liquid phase, but its viscosity at a lower temperature is higher.

Heavily loaded components performing reciprocating motions wear less when use is made of metal-cladding greases containing a metal power (for example, TsIATIM-203 grease with an admixture of 10% lead powder, etc.). They lacquer the protective coating and pick up gaps forming as a result of wear of the base material. Lead powder in the composition of the grease

is most effective in friction of steel against bronze, and bronze powder, in friction of steel against steel.

Heavily loaded reduction and worm gear mechanisms of the steering gear and landing gear retraction of heavy airplanes operate on TsIATIM-208 oil, which is dark-brown in color. At positive temperatures, it is a viscous liquid, and at negative ones, it has the usual consistency of plastic greases. It consists of a mixture of unrefined petroleum oils (axle oil, used for railroad rolling stock, and nigrol, used in automobile and tractor transmissions) and a thickener - calcium soap of sulfurized naphtenic acids and oxidized petrolatum. All the components of this grease are characterized by a marked adhesiveness, and the sulfur which it contains is the chief carrier of its antiseize properties. TsIATIM-208 grease is useful in the temperature range from -40 to 100°C.

In the drive of aviation starter generators, engine mountings, and in the lubrication of cables in a flexible casing, use is made of USSA graphite grease, the product of thickening of high-viscosity petroleum oils with calcium soap and 10% flake graphite. Because of the low thermal stability of calcium soap, the maximum operating temperature of this grease is of the order of 65°C (dropping point not below 77°C). The grease is suitable only for coarse mechanisms, as the mechanical impurities present in flake graphite cause a significant wear of the lubricated parts [18, 65, 96].

Instrument Greases

OKB-122 plastic greases of various brands are intended for aviation instruments and special equipment. Their composition includes low-freezing

polysiloxane oils OKB-122, very stable in long-term operation, and moisture-resistant thickeners such as lithium stearate and other nonhygroscopic soaps, and ceresin. Like the corresponding oils, they are efficient at very low temperatures (-70°C and below). The upper limit of their working temperature is determined by the thermal stability of the thickener: 140°C for grades OKB-122-7 and OKB-122-7-5, and 70°C for grades OKB-122-8 and OKB-122-12. Greases OKB-122-7 and OKB-122-12 are distinguished by the strength of their boundary film; they are used for worm gear and other loaded mechanisms for controlling airplanes and electric drives. OKB-122-7-5 grease, with a low ultimate strength and low viscosity, is used in high-speed low-load components of gyromechanisms. OKB-122-8 grease is used in other components of sighting and electronic equipment and instruments. Grease 2TsPK, consisting of MVP oil and ceresin with an admixture of bone oil, is intended for photographic equipment, autopilots, and compasses [59, 81].

Greases for Corrosive Media

Special greases are designed for high-speed friction components operating in contact with corrosive ingredients. They are prepared from synthetic oils, i.e., diester, fluorocarbon, or fluorochlorocarbon oils. For example, the soft VNII NP-223 grease, which has a low viscosity in service and is based on dioctyl sebacate and thickened with sodium soap and sodium nitrite, provides lubrication of antifriction bearings with a speed up to 60,000 rpm. Its dropping point is not below 175°C ; the grease is toxic [17, 59, 72, 96].

SEALING GREASES

BU Grease

Gasoline-resistant BU sealing grease is used for packing and sealing joints and cocks of fuel, oil and hydraulic systems. It consists of oxidized castor oil and zinc soap prepared from castor oil, and a small amount of glycerin (4%). This grease does not dissolve in hydrocarbons and adheres well to metals; it is low-melting (dropping point, 55°C). In winter, BU grease thickens, and before being applied, should be diluted with alcohol (up to 25%) [59, 72].

MGS Grease

MGS grease, which is grey in color, is used for sealing cocks, gaskets, and threaded joints of anti-icing systems and other installations containing alcohol, glycerin or water. It consists of transformer oil and barium soap, which is insoluble in water and other polar liquids. Its dropping point is 110°C; the grease is softer than BU. It is unstable to the action of fuels and oils. Because of its low colloidal stability, MGS grease becomes useless after approximately six months [72].

TsIATIM-205 Grease

TsIATIM-205 grease, prepared from highly refined petroleum oils (vaseline, medical and cosmetic oils) and ceresin (43-47%), is used for threaded joints of pipelines and fittings in contact with corrosive components. It prevents

the joints and cocks from sticking. The grease is relatively low-melting (dropping point, 65°C) and white or light cream in color. It is marked by a high impermeability to moisture, and for the same layer thickness, allows approximately 100 times less moisture to pass through than TsIATIM-201 grease [17-72].

GREASES FOR PRESERVATION

External Preservation

Protective greases for external preservation of equipment, individual parts and materials should be viscous and capable of being held on the lubricated surface, highly resistant to moisture and impenetrable to it, and stable at room temperature. Their fusion temperature should be sufficiently low to allow a simple application on the heated surface to be protected (by means of an atomizer, brush, or dipping).

Two greases commonly employed for external preservation are UNZ (universal, low-melting, protective) gun grease and UN (universal, low-melting grease) technical vaseline, which are products of melting of high-viscosity petroleum oil with solid hydrocarbons - petro'atum, cerasin, and paraffin (the amount of thickener is up to 75%). About 0.02% of sodium hydroxid is added to the gun grease. The hydroxide neutralizes the acid products, dangerous from the standpoint of steel corrosion, formed during prolonged storage; the hydroxide itself does not react with steel. Gun grease is used for preserving steel products having no paint and varnish coatings. Technical vaseline, which contains no alkali, is used mainly for preserving nonferrous metal products

(zinc-plated, cadmium-plated and other products with coatings) and for application on polychlorovinyl protective covers. Both greases are moisture-resistant; their permeability to moisture is approximately 1/10 that of TsIATIM-201 grease. The effectiveness of the applied coatings ranges from 1-2 years in open air to several years under warehousing conditions.

Gun grease and technical vaseline melt at comparatively low temperatures (50-55°C), and their temperature of creeping down a vertical surface may be even lower (32-36°C). Although a thin continuous layer remains on the lubricated surface after creeping, it is insufficient to protect the surface from atmospheric corrosion. Improved PVK grease contains 1% of MNI-7 additive (oxidized ceresin), which raises the creeping temperature by 12-15°C and decreases the moisture permeability. Products under this grease are stored without manifesting corrosion several times longer than under UNZ gun grease. The advantages of PVK grease under tropical climatic conditions are unquestionable.

Reliable protection from the corrosive action of water, including seawater, is provided by AMS-3 grease, consisting of a high-viscosity oil and aluminum soap. It is thermally more stable than vaseline and gun grease (dropping point 95°C), and has a greater adhesiveness [17, 53, 65].

Internal Preservation

Liquid preservation lubricants containing small amounts of thickener but activated with various additives are convenient for internal preservation of systems and cavities of engines and their accessories. They provide protection

from corrosive substances contained in residues of spent oil, special liquid, fuel, and also in the sediment, carbon deposit, etc. To ensure a simple deslushing, they should be soluble in the working liquids of the corresponding installations and systems. Like all preservation greases, they should be adhesive and stable.

Widely employed has been K-15 grease, a dark-brown oily liquid consisting of MS-20 oil (55-60%) and transformer oil (up to 40%), thickened with moisture-resistant lithium soap (about 2%). It includes synthetic rubber (1%) for better film formation and the TsiATIM-339 additive (1%) containing compounds of phenols with sulfur and barium. The additive acts on the metal, promoting the formation of a protective film, neutralizes acidic organic products, and also prevents the deposition of oxidation products on the surfaces and the decomposition of oil or fuel. K-15 grease may also be used for external preservation of engines.

K-17 and K-19 (K-17n) greases differ from K-15 grease in the fact that they contain an antioxidant additive, diphenylamine (0.3%), and additional anticorrosive additives, calcium sulfonate (10% in K-17 additive) or sodium nitrite (2% in K-19 additive). The latter is effective under high temperature and high humidity conditions, where the ingredients of K-15 and K-17 greases do not provide sufficient protection from corrosion. MS-20 or MK-22 oil thickened with 6-10% ceresin may be used as replacement - a standby preservation grease for the inner cavities of engines [59, 65, 72].

TECHNICAL FLUIDS

APPLICATION AND CLASSIFICATION OF TECHNICAL FLUIDS

In aviation, technical or special fluids is the term applied to all liquid products of various compositions, other than fuels and lubricants, used in the operation of aviation technology. They include the working fluids of hydraulic systems and installations, i.e., hydraulic oils, aircraft anti-icing fluids, liquid fire-extinguishing compositions, cooling liquids for engines air-conditioning systems and other aircraft equipment. They also include fluids for ground servicing of aviation equipment - for control of ground icing, for the washing of systems, and technological solvents, used in manufacturing and maintenance, etc. A model diagram of the classification of special fluids is shown in Fig. 55.

Occasionally, anti-icing, anti-knock and other additives are inaccurately classified as special fluids, and liquid additives are classified as oils, etc. It is useful to consider such fluids, which are not used individually, as ingredients of fuels and oils.

The chemical composition of technical fluids is chosen so that the specific operating conditions of various types of equipment are met to the maximum extent [59, 72].

FLUIDS FOR HYDRAULIC SYSTEMS OF AIRPLANES AND HELICOPTERS
(HYDRAULIC OILS)

Operating Conditions

Airplane hydraulic drives, which control the vanes and ailerons, the retraction and extension of the undercarriage, flaps and air brakes, the control of the power plant units, armament, electronic equipment, wheel braking, and also the hydropneumatic shock absorbers of the undercarriage, are usually designed for the use of a single working fluid - the hydraulic fluid. In some cases, owing to a convenient arrangement of the corresponding hydraulic units, fuels and lubricating oils are simultaneously used as the working fluid (chiefly in the hydraulic automatic system of the engine and propeller).

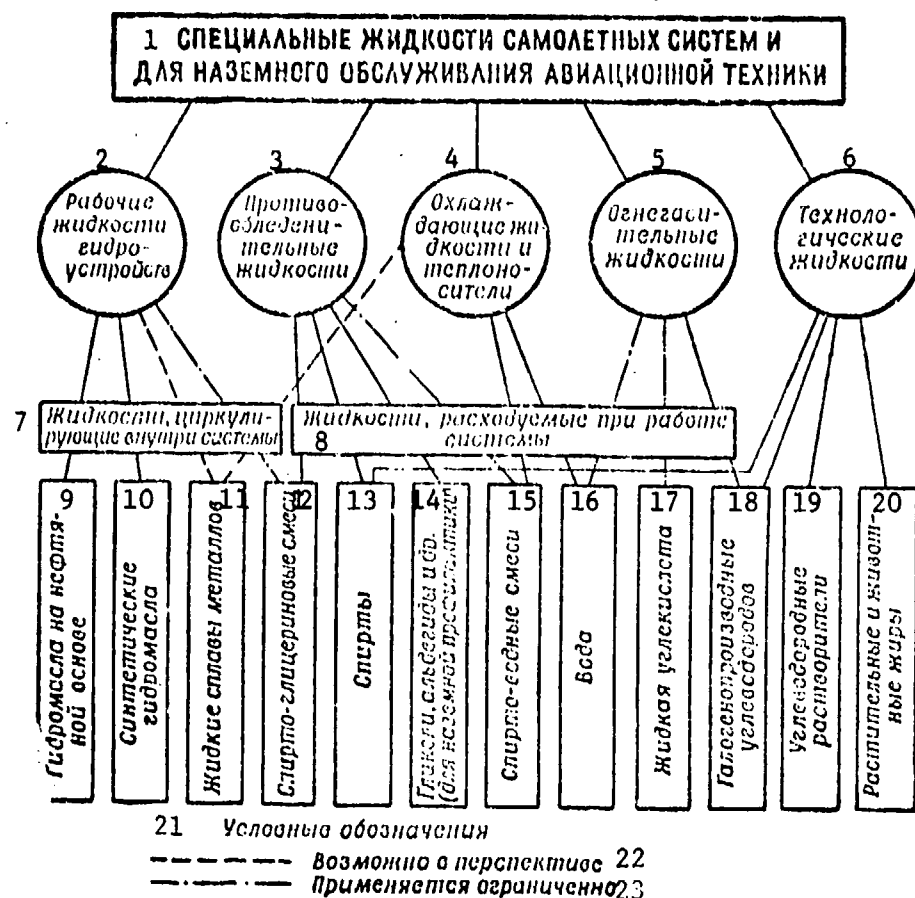
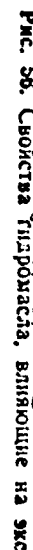


Fig. 55. Classification of special fluids for aeronautical equipment. Key:

1. SPECIAL FLUIDS OF AIRPLANE SYSTEMS AND FOR GROUND SERVICING OF AERONAUTICAL EQUIPMENT; 2. Working fluids of hydraulic systems; 3. Anti-icing fluids; 4. Cooling fluids and heat carriers; 5. Fire-quenching fluids; 6. Technological fluids; 7. Fluids circulating inside a system; 8. Fluids consumed during the operation of a system; 9. Petroleum-base hydraulic oils; 10. Synthetic hydraulic oils; 11. Liquid metal alloys; 12. Alcohol-glycerin mixtures; 13. Alcohols; 14. Glycols; aldehydes, etc. (for ground preventive maintenance); 15. Alcohol-water mixtures; 16. Water; 17. Liquid carbonic acid; 18. Halo derivatives of hydrocarbons; 19. Hydrocarbon solvents; 20. Vegetable and animal fats; 21. Notation; 22. Prospective; 23. In limited use.

A typical diagram of a hydraulic system of an airplane with indication of the characteristic operating conditions of its components - pressure, temperature, contact of working fluid with gases - is shown in Fig. 56 (of the large number of actuating pipelines, the diagram shows only one, the stabilizer booster pipeline, as an example). The conditions of the working fluid are fairly complex: the pressure in the system is up to approximately 200 atmospheres, and in the operation of certain hydraulic units, it sometimes rises sharply to 250-400 atmospheres; the temperature of the liquid may fluctuate from the minimum temperature of ambient air, -60°C , to $100-150^{\circ}\text{C}$ and above, due to friction during the operation of hydraulic devices, aerodynamic heating of the airplane, and heat transfer from the engine. The pressure in the hydropneumatic undercarriage shock absorbers during the landing of certain airplanes reaches 1000 atmospheres for a brief period; in this process, the fluid comes in contact with a gas being heated up sharply.



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Fig. 56. Properties of hydraulic oil affecting the operational reliability of the hydraulic system of an airplane. Key:

1. Operating conditions in components of hydraulic system; 2. Hydraulic oil quality indices (grouped according to the components of hydraulic system in which their influence is manifested); 3. Processes, effects and parameters directly dependent on the properties of hydraulic oil; 4. Dangerous aftereffects and service characteristics which may be caused by unsatisfactory quality of hydraulic oil; 5. Drainage line; 6. Idling; 7. From other mechanisms; 8. $1.5-2 \text{ kg/cm}^2$; 9. Up to 250 kg/cm^2 ; 10. Nitrogen; 11. Gaps $\sim 10 \mu$; 12. Up to $150-200^\circ\text{C}$; 13. Airplane stabilizer; 14. Stick; 15. Air; 16. $5-10 \mu$ opening; 17. $100-250 \text{ kg/cm}^2$; 18. From 60 to $+150^\circ\text{C}$; 19. Pipelines (up to $2-5 \text{ km}$); 20. Force main; 21. To other mechanisms; 22. TANK; 23. HYDRAULIC PUMP; 24. FILTER; 25. RELIEF UNIT, VALVES, THROTTLES; 26. HYDRAULIC ACCUMULATOR; 27. DISTRIBUTOR (AIR SLIDE VALVE); 28. HYDRAULIC DRIVE (BOOSTER); 29. Failure of all hydraulic drives; 30. Entry into the system; 31. Freezing point; 32. Boiling point; 33. Homogeneity of the fluid throughout the system; 34. Physical stability (phase separation tendency); 35. Irregularity of operation of hydraulic drives; 36. Accumulation of foam in tank; 37. Foaming tendency; 38. Water; 39. Pressure fluctuation; 40. Cavitation; 41. Solubility of gases; 42. Vaporizability; (flash point); 43. Erosion; 44. Failure of hydraulic pump; 45. Friction wear and seizure of gears; 46. Lubricating capacity; 47. An seize properties; 48. Viscosity; 49. Abrupt operation of hydraulic drives; 50. "Grinding" of additive, decrease in viscosity of hydraulic oil; 51. Stability of viscous additive; 52. Escape of hydraulic oil through seals; 53. Clogging of filter with solid particles; 54. Mechanical impurities; 55. Thermal stability; 56. Local overheating of hydraulic oil in individual components; 57. Clogging of filter with crystals at low temperature; 58. Water; 59. Temperature of start of crystallization; 60. Pressure drop, slow operation of hydraulic drives; 61. Pumping through the system; 62. Viscosity at low temperatures; 63. Possibility of ignition in the presence of breakdowns, cracks, leaks in joints; 64. Combustibility; 65. Flash point; 66. Fire; 67. Self-ignition temperature (in the presence of hot surfaces); 68. Explosion of hydraulic accumulator (undercarriage strut); 69. Possibility of self-ignition on sharp compression or heating; 70. Vaporizability; 71. Self-ignition temperature of vapor (in the presence of oxygen); 72. Failure of hydraulic accumulator; 73. Warping or destruction of seals; 74. Attack of rubber and other sealing materials; 75. Piston sticking; 76. Corrosive activity; 77. Nonoperation of hydraulic drive; 78. Jamming of slide valve; 79. Mechanical impurities; 80. Thermal stability; 81. Oxidation stability; 82. Slow operation of hydraulic drive; 83. Clogging of distribution channels; 84. Increase at low temperatures; 85. Antioxidant additive; 86. Corrosive activity of hydraulic oil and oxidation products; 87. Water; 88. Action on sealing materials; 89. Abrupt operation of hydraulic drive; 90. Decrease at high temperatures; 91. Time of filling of working cavities; 92. Viscosity-temperature characteristic; 93. Thermal degradation of additive, decrease in viscosity of hydraulic oil; 94. Stability of viscous additive; 95. Mechanical impurities; 96. Thermal stability; 97. Lubricating capacity; 98. Viscosity; 99. Abrasive wear; 100. Friction wear; 101. Corrosion wear; 102. Failure of hydraulic drive; 103. Deposits on surfaces; 104. Warping or destruction of seals; 105. Corrosive activity; 106. Oxidation stability; 107. Antioxidant additive; 108. Action on sealing materials.

3
1
To prevent oxidation and explosion of vapor of the working fluid (if it is hot) in shock absorbers and piston hydraulic accumulators (Fig. 56), chemically inert nitrogen is usually employed; it should be kept in mind that commercial nitrogen frequently contains a few percent of oxygen. In containers fed by the engine compressor, above the liquid, there is air whose oxygen dissolves in the liquid to some extent. The working fluid has a large relative area of contact with the metal walls, rubber and sealing materials, since its quantity is small (from a few liters to several tens of liters), and the surface of the inner cavities, particularly hydraulic lines, is considerable (in certain types of airplanes, the length of the lines reaches several kilometers) [63].

Principal Requirements

1
To provide for a sufficiently rapid response of the hydraulic units and their efficiency over a wide temperature range, the fluid used in them should have a moderate viscosity, a mildly sloping viscosity-temperature characteristic, a high boiling point, and a low freezing point. However, a high viscosity of the fluid is desirable to ensure a smooth motion of the parts of hydraulic units and prevent leaks and losses through seals. Hence, the selection of the viscosity of the fluid for hydraulic systems and the selection of the viscosity of lubricating oils should be a compromise. It is assumed that in the working temperature range, the viscosity of the fluid must not exceed the range of 8-1500 cS.

1
The fluid must not decompose, separate into layers, or evolve any substances capable of clogging the channels of the hydraulic systems, and likewise at high temperatures, i.e., it should be thermally stable. It should be safe

in regard to metal corrosion, swelling and destruction of rubber, plastic and leather seals, hoses, etc. Since it plays the part of a lubricant for rubbing parts of hydraulic devices, it should possess a good lubricating capacity (adhesiveness). It should not contain readily boiling ingredients, both from the standpoint of preventing losses, and in connection with the possible appearance of vapor-air lock, in order to avoid an irregular operation or breakdown of the hydraulic devices. It is desirable that the liquid be non-combustible, and its vapor, nonexplosive.

The same Fig. 56 enumerates the properties of hydraulic oil affecting the efficiency and service reliability of hydraulic equipment, and notes possible aftereffects of unsatisfactory quality of hydraulic oil. However, a real hydraulic oil (as well as fuel and lubricating oil) cannot satisfy all the requirements simultaneously. In practice, the hydraulic oils used are fluids which satisfy the most important requirements [59].

AMG-10 Hydraulic Oil

Airplane hydraulic systems use chiefly AMG-10 hydraulic oil, a hydraulic aviation oil with a viscosity not below 10 cS at 50°C and a red color. It is obtained by thickening the 210-320°C heavy low-paraffin kerosene fraction with a high-molecular-weight polymer, Vinypol, in much the same way as thickened lubricating oils (see Fig. 43). This provides for a sufficiently high viscosity level at positive temperatures in combination with a mildly sloping viscosity-temperature characteristic and a very low solidification point of the hydraulic oil (below -70°C). This ensures a normal operation of hydraulic units at high as well as low temperatures. The lubricating capacity of AMG-10

hydraulic oil is completely adequate for preventing the wear of hydraulic systems. In order to ensure stability for a long service period (two to three years), unsaturated hydrocarbons are removed from the petroleum base of AMG-10 hydraulic oil, and an antioxidant additive is introduced.

Mainly aromatic hydrocarbons are removed from AMG-10 hydraulic oil; for this reason, it causes swelling and corrosion of rubber and leather to a lesser extent than other petroleum liquids. In addition, hoses, seals, and cups of hydraulic systems are made of unstable rubber. However, during prolonged operation (usually, longer than two years), because of the wear and dissolution of the rubber ingredients, lumps sometimes appear in the fluid that may cause failure of the hydraulic devices. It is therefore necessary to replace the fluid at the right time. Another change occurring in AMG-10 hydraulic oil during service is a decrease in its viscosity due to gradual degradation ("grinding") of the viscous additive. This leads to an excessively coarse operation of the mechanisms, for example, to an abrupt operation of the brakes, and in some cases, to leakage of the oil inside the hydraulic devices or leakage to the outside. If the viscosity drops below 8 cS, the hydraulic oil should be replaced without waiting for the established service life to be reached.

Malfunctions in the operation of hydraulic devices (slow response of brakes, delay in the extension and retraction of flaps and undercarriage) may be due to separation of dissolved water, which had entered the fluid from air, out of the liquid, and its freezing on the filter, in the reduction valves of the hydraulic system, slide valves, etc. Despite the precautions taken during filling (the last 150-200 ml which may contain settled water is

left in each can), water in hydraulic oil may show up in the course of service as a result of dissolution of atmospheric moisture in contact with the fluid in the hydraulic tank. Periodic checking for the absence of water in the lower points of hydraulic systems is therefore necessary.

An important disadvantage of petroleum-base hydraulic oil is its flammability and a thermal stability inadequate for prospective airplanes. When the hydraulic system of an airplane is damaged, the fall of hydraulic oil on hot parts of the engine causes it to ignite, which may lead to a fire. The danger is aggravated by the fact that the hydraulic oil is ejected under high pressure. Prolonged action of high temperature (above 105°C) causes reappearance of a solid residue (the same as in the fuels). The penetration of its particles into the clearances of slide valve and other control units may lead to failure of hydraulic drives; into clearances of power units, to their premature wear; and deposition on filters, to a slowdown in the operation of hydraulic mechanisms [59, 66, 72, 81].

High-Temperature Fluids

In order to guarantee the reliability of operation of a hydraulic system at high temperatures, thermally stable organosilicon hydraulic oils have recently been under development abroad. In solidification temperature and viscosity-temperature characteristic, they surpass petroleum hydraulic oils, and are considerably better in thermal stability: there are samples which withstand a temperature of 200°C and higher for long periods of time. The insufficient lubricating capacity of organosilicon hydraulic oils may be reflected in the service life of gear pumps and other hydraulic mechanisms in

which there are high contact pressures during friction. In order to prevent their rapid wear, to some organosilicon fluids is added a diester oil which has a high lubricating capacity, a sufficient thermal stability, and does not adversely affect the viscosity-temperature characteristic. Such a composition is that of 7-50S-3 hydraulic oil.

Because the temperature conditions of operation of hydraulic systems will become more drastic in the future, fluids will be needed which will be efficient up to 500-700°C. They can scarcely be obtained from an organic base. An original solution to the problem may be the use of a eutectic alloy of alkali metals with a subzero melting point as such a working fluid. Such alloys have a very high boiling point and do not decompose in the liquid state; their viscosity is close to that of water. Their great disadvantage is a violent reaction with water and the necessity of having an absolutely sealed system filled with an inert gas to avoid oxidizing the alloy [40, 59, 70, 81, 96].

ANTI-ICING AND COOLING AVIATION FLUIDS

Operating Conditions and Requirements

In flights at subzero temperatures under high-humidity atmospheric conditions, on contact with the surface of an airplane or helicopter, the supercooled water droplets suspended in the atmosphere (their temperature may be considerably below 0°C, down to -20°C and even to -40°C) instantaneously crystallize and adhere to the surface, i.e., the aircraft becomes coated with ice. Icing may also occur when a very cold airplane enters a warm air zone (as a result of condensation of vapor and formation of frost).

One of the methods of combating the icing of airplanes and helicopters consists in supplying an anti-icing fluid to areas whose icing is most dangerous or takes place most rapidly (cabin glass panes, blades of helicopter rotor). The fluid moves toward the protected parts through small openings in specially placed tubes, to which it is supplied by an electric pump. Its flow rate usually amounts to several liters per hour.

The chief requirements for an anti-icing fluid are a low freezing point both in its natural form and in a mixture with water, an ability to readily dissolve ice and water, to wet the surface of metal and glass, and a sufficient mobility at low temperatures [59, 81].

Ethyl Alcohol

Rectified ethyl alcohol is predominantly used as an anti-icing fluid for cabin glass. It is used mainly because it completely satisfies the above-indicated general requirements, and in addition, is transparent, colorless, and marked by a very low freezing point (-114°C). Its mixtures with water also do not freeze at fairly low temperatures (Fig. 57). Alcohol wets metal and glass well, providing for the formation of a thin surface film on them; it dissolves ice, is stable, and does not leave dirt on the cabin windows. When an alcohol-water solution is formed, electrostatic bonds arise between the polar molecules of alcohol and water. This evolves heat, the solution heats up, and its volume decreases (Fig. 57). Thus, if 60 l of anhydrous alcohol is mixed with 40 l of water, after cooling to 20°C , the volume will not be 100 l, but only 93.31 l (3.69 l smaller).

Absolute (100%) ethanol boils at 78°C, and its density is 0.789. Because of the decrease in volume on mixing with water, the density of alcohol-water solutions is higher than the arithmetic mean calculated from their composition (Fig. 57). The experimentally determined dependence between the composition and density of alcohol, first established by D. I. Mendeleev, makes it possible to measure the strength of the alcohol (volume percent of pure C_2H_5OH contained in the solution) from the depth of immersion of the alcohol-meter, an instrument operating on the principle of the areometer (see Fig. 8).

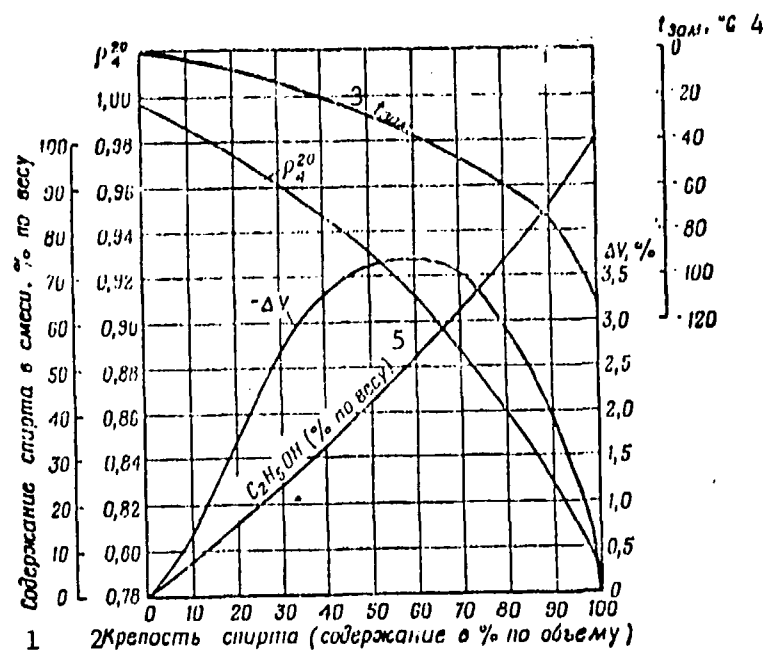


Fig. 57. Density ρ_4^{20} and freezing point t_{fr} of mixtures of ethanol and water; $-\Delta V\%$ -volume decrease on mixing (in liters per combined 100 l of alcohol and water before mixing) Key:

1. Alcohol content of mixture, % by weight;
2. Alcohol strength (content in vol. %;
3. t_{fr} ; 4. t_{fr} , °C; 5. (% by weight)

Rectified alcohol, used as an anti-icing fluid, contains 95.5-96.0% of anhydrous alcohol by volume; the preparation and preservation of alcohol of higher concentration involves technical difficulties. To economize the alcohol during training, alcohol-water mixtures of different compositions are used in certain cases. The chief disadvantage of ethyl alcohol as an anti-icing fluid is its corrosiveness (particularly toward zinc and aluminum). If the tanks and other elements of the alcohol system are made of aluminum alloys, the reaction with alcohol forms a gelatinous mass of metal alcoholates which clogs the system. The alcohol is passive toward steel and iron. Another disadvantage of alcohol is its fire hazard. In addition, alcohol evaporates rapidly; at the instant it leaves the holds, because of its low viscosity, it is easily blown off by an air stream. This makes its use difficult in combating the icing of propeller blades [59, 72, 86].

Alcohol-Glycerin Mixture

A mixture of 85% rectified alcohol and 15% glycerin, with a density of 0.8676, is used as the anti-icing fluid for helicopter blades. It differs from alcohol in a high viscosity and slower evaporation. As a result, it coats the helicopter rotor blades better. The freezing point of this liquid is not above -70°C . However, on oxidizing, glycerin may form crystals, clogging the holes.

In controlling the icing of airplanes on the ground (formation of frost, freezing of snow), use is made of EAl fluid (ester-aldehyde fraction) with an admixture of 5% gasoline and "Arktika" fluid (with ethylene glycol base) [1, 59].

Cooling Fluids

Fuel is used in modern supersonic airplanes as the cooling liquid for a number of systems and devices requiring a continuous removal of heat (oil radiators, cooling jackets of radio and engineering equipment). However, certain types of airplanes use a special reserve of cooling fluid in the cabin's air conditioning system. Since the compressed air fed into airplane cabins has a high temperature when it leaves the engine compressor, it is cooled in a special cooling turbine before entering the cabin. This cooling is insufficient in certain types of airplanes; before being fed to the cooling turbine, the air is cooled in evaporators. The cooling fluid in the evaporators is distilled water in summer, and a low-freezing mixture of 40-50% ethyl alcohol and 50-60% distilled water in winter. This mixture is injected into an evaporator through which runs a coil pipe carrying the air entering into the cabin.

The usefulness of distilled water in such systems is due to the fact that of all liquids, water has the maximum heat of vaporization (500-600 kcal/kg depending on temperature). The need for a preliminary distillation is due to the fact that natural water contains calcium salts, which after the evaporation of water in the airplane system would produce deposits (scale) on the coil pipe that would sharply decrease the heat transfer.

Normal operation of the water or water-alcohol system at altitude makes it necessary to produce excess pressure in this system. At an atmospheric pressure of 50 Torr, corresponding to an altitude of about 19 km, water boils already at 40°C. Finally, it should be kept in mind that at 0°C, on freezing,

water increases in volume by 10%, and the ice formed ruptures the pipelines, cavities, etc. [59].

FIRE-EXTINGUISHING COMPOSITIONS

Methods of Extinguishing Flames

Fire safety systems in airplanes and helicopters consist of a cylinder with a fire-quenching composition, pipelines and sprayers through which the composition is ejected in order to extinguish flames in parts of engines, fuel tanks, etc. When the cylinder is filled, a gas pressure necessary for ejecting the composition is produced by it.

Flame extinction during a fire may be achieved in various ways: insulating the combustion kernel from access of air, diluting the burning mixture with a neutral gas down to the lower limit of combustibility ("depleting" the mixture), sharply cooling the flame jet, and finally, by chemical intervention, in particular, by using a process which competes with combustion and ties up the combustible elements.

During the quenching of a fire, water and carbon dioxide, which is first liquefied at a pressure of over 60 atmospheres, have all of the above features, with the exception of the last. However, the fire-quenching concentration of carbon dioxide is high (to quench a flame, it must be present in the amount of 22% by volume in air); the required weight of carbon dioxide (together with the fire-extinguishing equipment) is too large. Water is altogether ineffective in quenching petroleum fuels; it causes spattering of the burning fuel and

and promotes spreading of the flame, and the fuel rises to its surface and continues to burn.

Halo Derivatives of Hydrocarbons

The most suitable fire-quenching agents are bromo derivatives of hydrocarbons. Decomposing at a high temperature, they are the source of atomic bromine, which at the instant of formation reacts more actively with combustible elements than atmospheric molecular oxygen. The heat of oxidation of hydrogen and carbon by bromine is tens of times smaller than by oxygen, the flame temperature drops, and the flame disappears. An essential role is played by the high vapor density of halo derivatives of hydrocarbons; they settle in the flame kernel zone.

The best flame-quenching liquid used at the present time is freon 114Br - tetrafluoroethane $\text{C}_2\text{F}_4\text{Br}_2$ (its active flame-quencher is bromine; fluorine remains bound to the carbon skeleton). Its boiling point is 46°C , and freezing point, -112°C ; it has no corrosive effect on materials.

Widely used are the well-known flame-quenching compositions "3,5" (a mixture of 70% ethyl bromide $\text{C}_2\text{H}_5\text{Br}$ and 30% liquid carbon dioxide CO_2) and "7" (mixture of 75% dibromomethane CH_2Br_2 , 19% ethyl bromide $\text{C}_2\text{H}_5\text{Br}$, and 6% liquid carbon dioxide CO_2). The designation of these flame-quenching liquids by the numbers "3.5" and "7" indicates that their flame-quenching concentration and hence, consumption, is respectively 3.5 times and 7 times smaller than that of carbon dioxide, taken as the standard. A disadvantage of these compositions is their corrosiveness. All the bromo derivatives of

hydrocarbons, including freon 114Br, are toxic. They have still another disadvantage: Their prolonged contact with aluminum alloys sometimes leads to the formation of the pyrophores (self-igniting substances) trimethylaluminum and triethylaluminum, and to the danger of a spontaneous generation of a fire; thus the flame-quenching compositions are converted into their exact opposite [72, 81].

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**EQUILIBRIUM PENNY-LIKE CRACK IN
INDENTATION FRACTURE.**

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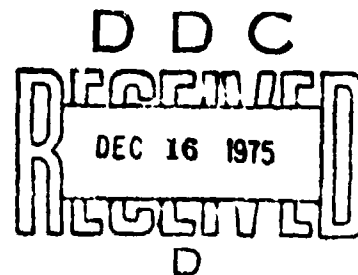


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ABSTRACT

A study is made of the mechanics of two basic types of indentation fracture, *cone cracks* ("blunt" indenters) and *median cracks* ("sharp" indenters). The common feature which forms the central theme in this work is that both crack types, in their well-developed stages of growth, may be regarded as essentially "penny-like". On this basis a universal similarity relation is derived for equilibrium crack dimension as a function of indentation load. Experimental measurements confirm the general form of this relation. A more detailed fracture mechanics analysis is then given, to account for additional, contact variables evident in the data. Notwithstanding certain analytical limitations, the study serves as a useful basis for investigating a wide range of contact-related problems, both fundamental and applied, in brittle solids.

1. INTRODUCTION

Considerable interest has recently been shown in the crack patterns produced during the indentation of brittle surfaces. Apart from providing a novel means for measuring important fracture parameters (e.g. fracture surface energies, crack velocities), the individual indentation fracture event serves as a convenient "basic microscopic unit" in the ultimate description of a wide range of ceramics engineering properties (degradation, abrasion, wear, erosion, etc.).¹ By far the greatest attention has been directed to the relatively well-defined crack configuration generated by a spherical indenter, the so-called Hertzian cone fracture.^{2,3} The sphere typifies "blunt" indenters, in which the contact prior to fracture remains predominantly elastic. By contrast, the more complex fracture patterns produced by "sharp" indenters (e.g. cone, pyramid),⁴ where limited irreversible flow about the indenter point occurs as a necessary precursor to crack growth, have gone largely unstudied. Yet of the two extremes in indenter geometry, it is the sharp indenter which emerges as more pertinent in real contact situations where severity of surface damage is a prime concern.^{5,6}

In this study we seek to establish a wider descriptive basis for the cracking that occurs in the general indentation of brittle solids, with particular emphasis on sharp indenters. For this purpose it becomes convenient to identify various phases in the evolution of the indentation fracture event, from crack initiation in the contact field to full-scale

propagation in the advanced loading (and even unloading) stages. While somewhat arbitrary, this approach usefully highlights the similarities and differences in the blunt and sharp indenter patterns, and permits an adequate description of certain facets of a given fracture situation in cases where the overall behaviour appears hopelessly complex. It is found that the greatest differences occur in the earliest stages of indentation, the very mode of crack initiation depending critically on the geometrical distribution of contact stresses. Conversely, the similarities become more apparent in the well-developed stages, in which the far field of the applied loading now controlling crack growth is insensitive to details in the contact region. Ultimately, all well-developed indentation cracks tend to expand on an ever-increasing, near-circular front at advanced loading, thus assuming a penny-like configuration. It is this last aspect which forms the focal point in the present work.

2. GENERAL FEATURES OF INDENTATION FRACTURE PATTERNS

Fig. 1 illustrates the essential features of crack geometry for both blunt and sharp indenters, along with the relevant fracture mechanics parameters. In each case the indenter sets up a contact stress field, the tensile component of which provides the driving force for the ensuing fracture. If the applied load P were to be effectively concentrated at a point in the specimen surface (i.e. $a \rightarrow 0$), the intensity of the stresses would vary according to a simple inverse-square relation (the so-called Boussinesq field).^{1,4} However, in reality the stress level cuts off

at some finite limit within the contact region: with blunt indenters the cutoff is merely a manifestation of a redistribution in load over a nonzero, elastic contact area, whereas with sharp indenters it is associated more closely with the inability of the solid to sustain stresses greater than some "yield" value⁴. One may accordingly view the real distribution of stresses along the prospective crack path in terms of a hypothetical superposition of Boussinesq stresses and localised, near-contact "closure" stresses.*

In this context we investigate the evolution of the two situations depicted in Fig. 1, as follows:

2.1 Blunt Indenters

(i) *Crack nucleation.* Outside the elastic contact circle (whose radius is determined by the load, indenter size, and elastic constants) the stresses in a shallow "skin" layer, where surface flaws pre-exist, are highly tensile.^{2,3,6} As the stress intensity builds up with increasing load, one or more of the flaws nucleates a crack.

(ii) *Crack formation.* The "dominant" flaw runs around the contact circle to form a shallow surface ring crack. Owing to the restraining action of the "closure" stresses, the newly formed ring does not, in general, extend spontaneously downward: the system must first overcome an energy barrier. Accordingly, the ring crack may be driven downward, either stably by purely mechanical forces (i.e. by increasing the indenter load)² or subcritically by combined mechanical and

* The procedure is strongly analogous to that used in fracture theory to represent the complex nonlinear stress field at the tip of a propagating crack.⁷

chemical forces (e.g. by introducing a reactive environment into the system)⁹, until some critical depth (typically $\approx 0.1 a$) is attained.

(iii) *Crack propagation.* Once beyond the critical, formation depth the surface ring propagates unstably into the full Hertzian cone, at a depth $\approx a$. The crack is then said to be "well-developed", in that details in the near-contact stress distribution no longer greatly influence the fracture mechanics. Increasing the driving force still further simply causes the cone to continue its propagation, in a stable manner.

(iv) *Crack unloading.* Upon unloading the system the cone crack tends to close (but rarely to heal).¹⁰ In certain contact situations frictional tractions between indenter and specimen may actually enhance growth of the cone system.¹¹

2.2 Sharp Indenters

(i) *Crack nucleation.* In this case the contact is partially plastic, necessarily so because of a singularity about the sharp indenter point in an otherwise linear elastic field.⁴ The plasticity somewhat relieves the tension locally about the contact area (whose dimension is now determined by the load, indenter shape, and material hardness). Instead, the greatest concentration of tensile stress occurs directly below the indenter point, and the crack nuclei are created there by the deformation process itself.

(ii) *Crack formation.* The deformation-induced crack nuclei grow as near-pennies, wholly contained beneath the contact zone, on median planes (planes containing the normal

load axis).⁴ As with the Hertzian surface ring fractures, these so-called median cracks grow stably, but are susceptible to environmental effects. Depending on the indenter geometry, this formation stage may continue to a depth $\approx a$ or more. Several, mutually intersecting median cracks may form during the course of indentation.

(iii) *Crack propagation.* At some stage in the growth the median cracks begin to "break through" to the specimen surface; the restraining, compressive "hoop" stresses outside the contact area can no longer contain the expanding pennies.⁴ This critical stage is not as well defined as the corresponding cone development in the Hertzian test, and the different co-existing median cracks may "pop-in" successively as the loading proceeds. The cracks then tend to the well-developed configuration of more or less symmetrical, stably propagating half-pennies centred on the contact point.

(iv) *Crack unloading.* Unloading the system causes the median cracks to close. However, with sharp indenters there are additional, residual-stress effects, attributable to incompatibility between the plastic zone and surrounding elastic material;¹² the mechanical mismatch appears to set up a "reversed field" just prior to complete withdrawal of the indenter. Thus the stresses which, on loading, acted to open up the median cracks, tend now to compression, thereby enhancing closure beneath the indenter. In the near-surface region, on the other hand, the reversal is of opposite sign, the development of a hoop tension actually opening up any partially contained penny cracks to the specimen surface.

The net result is therefore always a crack configuration close to the ideal half-penny shape, regardless of whether the fully propagating stage was reached during loading or not. A secondary manifestation of the residual stress field is the initiation of an entirely different, laterally extending system of cracks (not shown in Fig.1b); these lateral cracks emanate from the deformation zone and grow in a saucer-shaped configuration toward the specimen surface, corresponding to a "chipping mode" of fracture.¹²

3. SIMILARITY RELATIONS FOR THE PENNY-LIKE CRACKS

In the interest of simplicity we proceed to an analysis of the indentation fracture problem on the assumption that crack growth is determined predominantly by point-load, Boussinesq stresses. Such an assumption effectively restricts the applicability of any fracture mechanics solution to the fully-developed stages of crack propagation. Preceding, formation stages of crack growth may then be seen as precursor stages, in which the near-contact field exerts an initial perturbing restraint on the evolution of the fracture pattern.

With this simplification the way is open to an analysis in terms of a scaling argument, in which mathematical formalism may be conveniently circumvented. Roesler¹³ used this approach to obtain a solution for the cone crack configuration, and in the present section we merely generalise Roesler's treatment. The idea is to make use of the geometrical similarity of the well-developed cracks, in conjunction with the fundamental Griffith energy-balance condition for crack extension,¹⁴ to derive a relationship between the size of the cracks and the indenter load. In this way, noting that all well-developed

indentation cracks are of the same geometrical form, i.e. penny-like (in the sense that they extend on a near-circular front), we may obtain a general expression for equilibrium growth.

In accordance with the Griffith condition, one seeks the configuration for which the rate of increase of total surface energy just balances the rate of decrease of total mechanical energy as the crack expands. Since the area of the crack surface must scale with the square of the characteristic crack dimension, i.e. say, the total surface energy must be of the form

$$U_S = \Gamma a^2, \quad (1)$$

where Γ is the fracture surface energy. Again, we may note that the intensity of the indentation stress field will be determined by the point load divided by a characteristic area ($\propto P/a^2$), that the strain energy density will be given by the square of the stress divided by an elastic modulus ($\propto P^2/a^4 E$, with E Young's modulus), and that the volume of stressed material associated with the field of the crack will scale with the cube of the crack dimension ($\propto a^3$), such that the total mechanical energy may be written

$$U_N = P^2/Ea, \quad (2)$$

The energy-balance requirement, $dU_S/da = -dU_N/da$, then gives

$$P^2/a^3 = \text{const.} \quad (3)$$

for equilibrium cracks.

In the point-load approximation used here all details of the contact conditions are effectively "washed out".

However, we should expect the indenter size or shape to have some influence in the fracture mechanics, for, as we have seen, the very nature of the crack pattern (i.e. whether cone or median) is determined to a large extent by the contact geometry. Before taking up this issue in depth we shall first examine pertinent experimental data in connection with the verification of Eqn.3.

4. EXPERIMENTAL MEASUREMENTS OF CONE AND MEDIAN CRACKS

Observations have been made of the manner in which the size of both cone and median cracks depend on indenter load. All tests were conducted on soda-lime float glass, 12.7 mm thick, under conditions close to equilibrium (viz. under conditions effectively excluding water vapour from the cracks¹⁵). The progress of the cracks was followed either photographically or by travelling microscope; inaccuracies in the measuring techniques were found to be insignificant in comparison to the scatter in results from crack to crack.^{**} A considerably greater proportion of the experimental effort was devoted to the median cracks, these being relatively undocumented in the literature.

4.1 Cone Cracks

The cone crack tests were conducted within an environmental chamber, with the force on the indenter delivered

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As seen in the data of Figs.2 to 5 below. Together with the data points, these figures include least-squares fits of Eqn.3 (corresponding to a minimisation of the error in $P/c^{3/2}$); the slopes of the lines thus fitted have a typical standard deviation of 5%.

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by a dead-weight loading machine. The indenter itself was a tungsten carbide sphere, but with a polished flat of 1 mm rad. to maintain an invariant contact area (thus to ensure that the surface trace of the cone crack not be enveloped by an expanding contact circle). A light surface abrasion of the glass test slabs (e.g. in a slurry of No. 1000 SiC grit) prior to indentation served to introduce an abundance of suitable "pre-existing flaws" for crack initiation. The cracks were started by loading the specimens slowly, in moist air; this allowed for the controlled formation of well-defined surface rings, from which highly regular cones could be propagated. Having thus developed a crack, the chamber was evacuated ($\approx 10^{-4}$ Pa), and the base radius R of the stably propagating cone (representing the characteristic dimension c of Sect.3) recorded as a function of increasing load P .

Fig.2 shows the results, for four cracks. The plot is seen to be linear, within the scatter of the data. Eqn.3 thus adequately represents the fracture mechanics for cone cracks.

4.2 Median Cracks

For the median crack tests a standard Instron universal testing machine was used to deliver the indentation load. Indenters included six tungsten carbide cones ranging in half-angle from $\psi = 30^\circ$ to 80° in 10° intervals, and a conventional Vickers diamond pyramid in a heavy-duty mount. The glass surfaces were indented in their as-received state. Initial loading was slow, to permit the median cracks to be formed in a controlled manner. For the sake of reasonable speed in the data accumulation, all subsequent crack propagation measurements were made in normal laboratory test environment.

The first set of such measurements involved following the depth D of the dominant median crack as a function of steadily increasing load P . In these tests the crosshair of

a travelling microscope was continually translated to predetermined positions along the path of the expanding crack, and the load at the instant each crosshair position was reached by the crack tip appropriately recorded. This procedure conveniently provides the means for reducing the kinetic contribution to crack growth (due to the inevitable presence of water vapour) to a tolerably low level, through a simple adjustment of the Instron crosshead speed. For instance, with a crosshead speed of 0.5 mm min^{-1} in the present experiments kinetic effects were estimated to give rise to increases of considerably less than five percent in the crack lengths.***

The data obtained are plotted in Figs. 3 and 4. As with the cone crack data, these plots confirm the essential form of Eqn.3, within the limits of experimental reproducibility. However, certain additional features in the median crack results warrant further attention here. First, as a result of a greater variability in the crack pattern, the scatter in data becomes relatively pronounced at higher indentation loads. This trend could be directly associated with discontinuities in the downward growth of the leading median crack, corresponding to the sudden pop-in and expansion of intersecting neighbours. In general, the indentation process was typified by an extended sequence of abrupt load drops, these being most marked for the conical indenters of smaller half-angle. A second complicating feature was the tendency in the case of the most "blunt" conical indenter (i.e. $\psi = 80^\circ$) for cone crack formation to precede median cracking. Here the

*** As adjudged from comparison with control tests in dry nitrogen atmosphere, in which slow crack growth effects were imperceptible.

plastic component of the contact is relatively small, and the effectiveness of pre-existing surface flaws as nucleation centres for fracture accordingly matches that of the deformation-induced flaws. The presence of the enveloping cone crack noticeably restricted the development of the contained median pennies.

A second set of measurements, prompted by the observation (Sect.2.2) that any median cracks still in the formation stage tend to complete their development into the half-penny configuration during unloading, was taken from the residual crack patterns on the indented test surfaces. In these experiments the Instron crosshead velocity (0.5 mm min^{-1}) was simply reversed upon the attainment of some prescribed peak indentation load P' . The glass surfaces were then lightly etched in dilute hydrofluoric acid until the cracks were clearly visible, and the trace 2D' of the dominant median crack appropriately recorded for each indentation. Plots of the data thus obtained for conical indenters are given in Fig.5, and may be compared with their analogues of Fig. 3.

5. MORE EXPLICIT FRACTURE MECHANICS ANALYSIS

While the data of the previous section verifies the functional relationship between crack size and indenter load given in Eqn.3, our fracture mechanics description remains incomplete. The emergence of contact geometry as an important factor in Figs. 2 to 5 emphasises a major inadequacy in our simplistic treatment of Sect.3. To account for this additional factor a more detailed analysis is necessary. We adopt the conventional fracture mechanics approach here, seeking solutions for the crack-extension force G or stress-

intensity factor K , from which equilibrium equations may once again be obtained via the Griffith condition, expressible as $G = K^2(1-\nu^2)/E$ (plane strain).¹⁷

5.1 Cone Cracks

The case of well-developed cone cracks has already been treated rigorously in the paper by Roesler,¹³ and we shall do no more than quote Roesler's solutions. The crack-extension force, per unit width of crack front, is calculated as

$$G = \kappa_R^p(\nu) P^2 / ER^3 \quad (4)$$

where κ_R^p is a dimensionless constant uniquely determined by Poisson's ratio ν : the superscript p denotes a fully propagating crack and the subscript R identifies the characteristic crack dimension. In conjunction with the Griffith condition, Eqn.4 gives the equilibrium expression

$$P^2/R^3 = 2\Gamma E / \kappa_R^p(\nu) . \quad (5)$$

The dimensionless constant, although independent of the geometry of the indenter (provided the contact remains blunt), directly involves the cone crack angle α (Fig.1a) according to¹³

$$\kappa_R^p(\nu) = f(\nu) [\cos \alpha]_\nu . \quad (6)$$

This result therefore represents only a minor elaboration on the similarity relation, Eqn.3. A numerical analysis by Roesler for $\nu=0.25$ ($\alpha=22^\circ$) gives $\kappa_R^p=2.75 \times 10^{-3}$, whereas from the slope of Fig.2 we obtain for soda-lime glass, using $\Gamma=3.9 \text{ Jm}^{-2}$ and $E=7.0 \times 10^{10} \text{ Pa}$,¹⁸ the value $\kappa_R^p=(1.19 \pm 0.10) \times 10^{-3}$.

5.2 Median Cracks

For the median cracks we consider the centre-loaded half-penny configuration of Fig.1b. We envisage a single well-developed crack driven primarily by the wedging component of indentation force, P_{\perp} , normal to the median plane. In the case of a *smooth* contact the wedging force is readily resolved in terms of the characteristic half-angle ψ of the indenter,

$$P_{\perp} = P/2\tan\psi \quad (7a)$$

More generally, for a *rough* contact, Eqn.7a modifies slightly to

$$P_{\perp} = P/2\tan\psi' \quad (7b)$$

with

$$\psi' = \psi \pm \arctan \mu, \quad (8)$$

μ being the coefficient of sliding friction; the plus sign in Eqn.8 refers to the *loading* half-cycle, the minus sign to the *unloading* half-cycle. Contact friction may thus be regarded as either "blunting" (loading) or "sharpening" (unloading) the indenter.

The stress-intensity factor for the crack system under consideration is obtainable from fracture mechanics handbooks,¹⁹

$$K = 2P_{\perp}/(\pi D)^{3/2} \quad (9)$$

(This equation omits a small correction factor associated with free-surface effects.) Incorporating Eqns.7b and 9 into the Griffith condition, we have

$$P^2/D^3 = 2\Gamma E/\kappa_D^P(\nu, \psi') \quad (10)$$

in analogy to Eqn.5, with the dimensionless constant

$$\kappa_D^P(\nu, \psi') = (1-\nu^2)/\pi^3 \tan^2\psi'. \quad (11)$$

The geometrical term ψ' , unlike its counterpart α in the cone crack system, varies independently of ν . Using the values of ν , Γ and F already specified, we may evaluate $\kappa_D^P(\psi)$ for soda-lime glass from the slopes of Figs. 3 and 5, and thence investigate the validity of the present analysis by plotting $\arctan \{ [(1-\nu^2)/\pi^3 \kappa_D^P]^{1/2} \}$ as a function of ψ . According to Eqns. 11 and 9, such a plot should have a slope of unity and an intercept on the ordinate dependent on μ . However, the results of the present experiments, Fig. 6, are too uncertain to warrant an appropriate curve-fitting exercise; we recall in particular from Sect. 4.2 the tendency for the crack pattern to depart markedly from the ideal, single half-penny configuration at extremes in half-angle ψ . Instead, we simply plot the zero friction curve in Fig. 6 for comparison with the data.

6. DISCUSSION

Our treatment of the indentation fracture problem derives from the rationalisation that the well-developed cracks are basically penny-like in form. This is tantamount to assuming that the fracture mechanics are predetermined by a point-loading, Boussinesq-type stress field, in which case we should recognise certain limitations of the approach. For a start, as mentioned in Sect. 2, near-contact "closure" stresses operate to retard crack growth in the "formation" stage. The nature of these near-contact stresses determines, among other things, the "critical load" at which growth proceeds to the fully-developed stage^{2,4}. Thus, in using the present analysis to model ceramics engineering problems, we are restricted to the more severe indentation damage

situations. A second limitation concerns the fact that the Boussinesq picture appears to be inadequate for describing the lateral cracks which form upon unloading sharp indenters (Sect.2.2). Although its saucer-like geometry does preserve the most essential feature of the penny configuration (namely the outward expansion on a near-circular front), the lateral crack system evolves in an ill-defined residual stress field whose very source is not well understood.¹² This secondary crack type warrants further attention, for it relates closely to surface removal processes in brittle materials.^{1,20}

At the same time, our circumvention of detailed descriptions of the near-contact stresses in the loading half-cycle, and of the residual stresses in the unloading half-cycle, has not been entirely restrictive. We have still been able to identify some parameters associated with the nature of the contact, such as α in Eqn.6 for cone cracks and ψ and μ in Eqns.8 and 11 for median cracks, although the role of these parameters could not be unequivocally established in the present experiments. Again, due recognition has been given to the important function of residual stresses in expanding partially contained median penny cracks to the specimen surface, thereby permitting one to infer the relevant fracture mechanics from examinations of crack traces on test surfaces *after* indentation²¹; the potential application of this correlation as a means for diagnosing the history of indentation damage events in brittle materials, especially in opaque materials, becomes obvious.

Indentation fracture presents itself as a useful addition to the mechanical testing repertoire of the materials scientist.¹ Where the measurement of basic fracture mechanics parameters is the objective the theory given here should serve

as an adequate framework for analysing the data, provided the indentation conditions are chosen such that a single, well-defined penny crack is produced: the cone crack system appears to be best suited for this purpose. Although we have considered only equilibrium cracks, an extension of the analysis to include kinetic effects is not impracticable: indeed, cone crack tests have actually been used to obtain crack velocity data on glass in moist environments.²² Where an analysis of more practical contact damage situations is required one needs to bear in mind that the calculations are likely to overestimate the crack dimensions. This constitutes no real disadvantage in strength degradation studies, from which we emerge with a sound basis for conservative engineering design.^{5,6} Moreover, the distinction between blunt and sharp indenters, representing extremes in contact severity, provides convenient bounds for the description of real contact situations.

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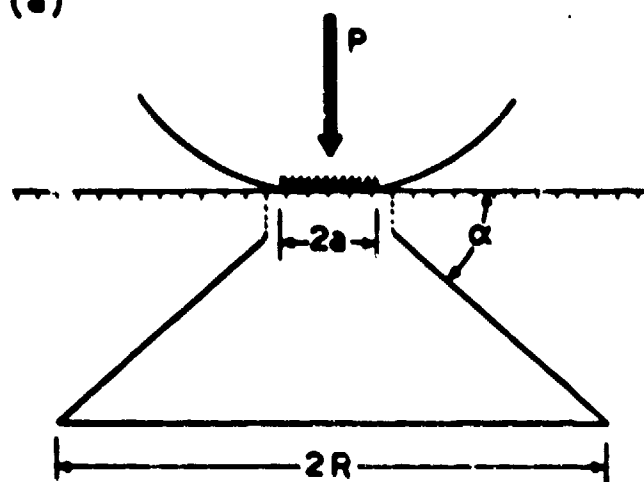
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FIGURE CAPTIONS

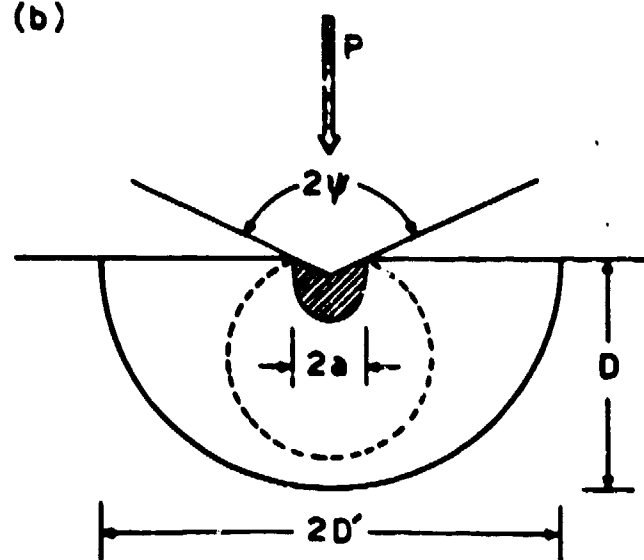
1. Basic indentation fracture systems. (a) Cone crack system, associated with "blunt" indenter: crack nucleates from pre-existing surface flaw (small dashes) outside contact (shaded), forms into surface ring (broken line), and finally becomes critical and propagates into fully developed cone. (b) Median crack system, associated with "sharp" indenter: crack nucleates from plastic contact zone (shaded), forms into contained penny (broken circle) and ultimately develops into full half-penny.
2. Results from observations of fully-developed cone cracks in soda-lime glass. Data points from vacuum tests, using truncated spherical indenter. Each symbol represents separate crack.
3. Results from observations of median half-penny cracks in soda-lime glass. Data points from tests in air, with crack dimension recorded directly as a function of increasing load. Conical indenters, with half-angles as indicated. Each symbol represents separate crack.
4. Results from observations of median half-penny cracks in soda-lime glass. Data points from tests in air, with crack dimension recorded directly as function of increasing load. Vickers pyramid indenter. Each symbol represents separate crack. Compare slope with those of Fig.3 (half-angle between opposing pyramid edges is 74°).

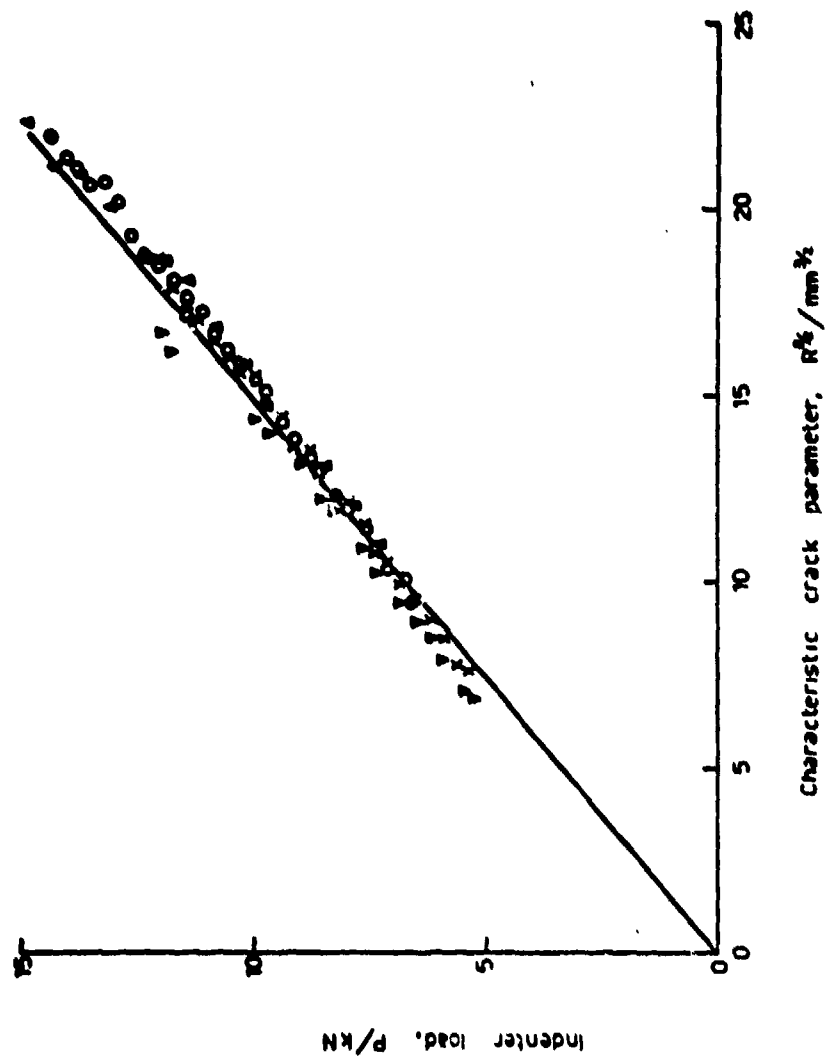
5. Results from observations of median half-penny cracks in soda-lime glass. Data points from tests in air, with crack dimension recorded from residual surface trace as function of peak load. Conical indenters, with half-angles as indicated.
6. Plot of median crack data to investigate the validity of Eqn.11.

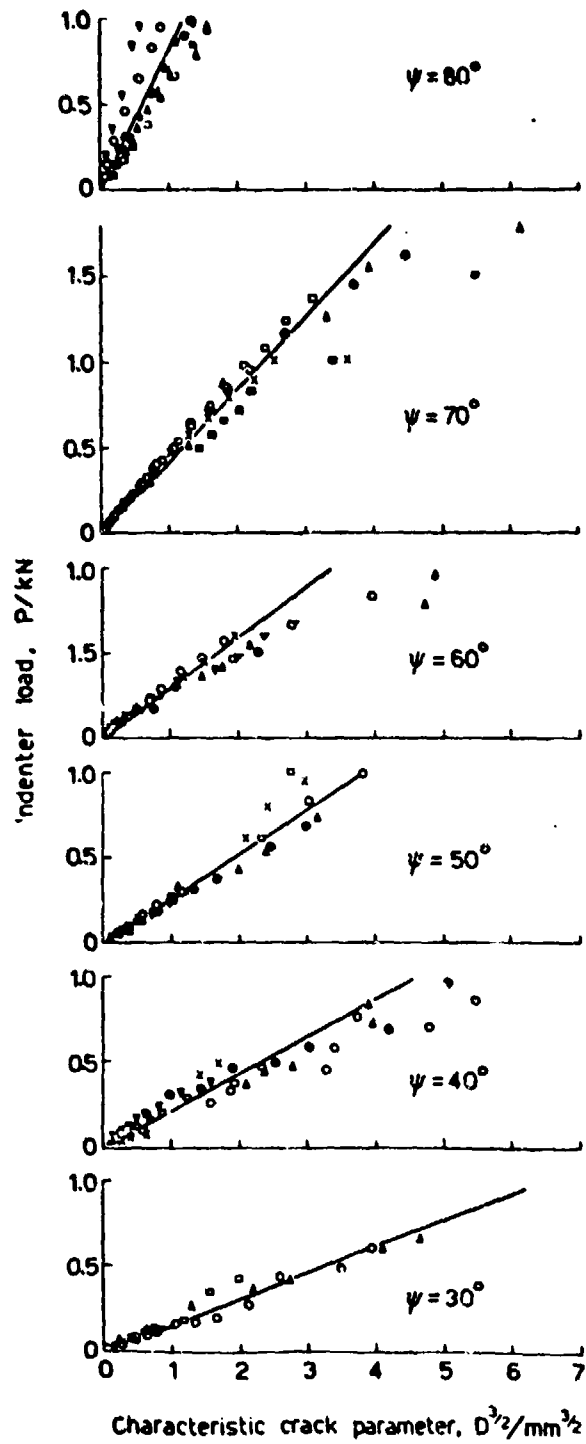
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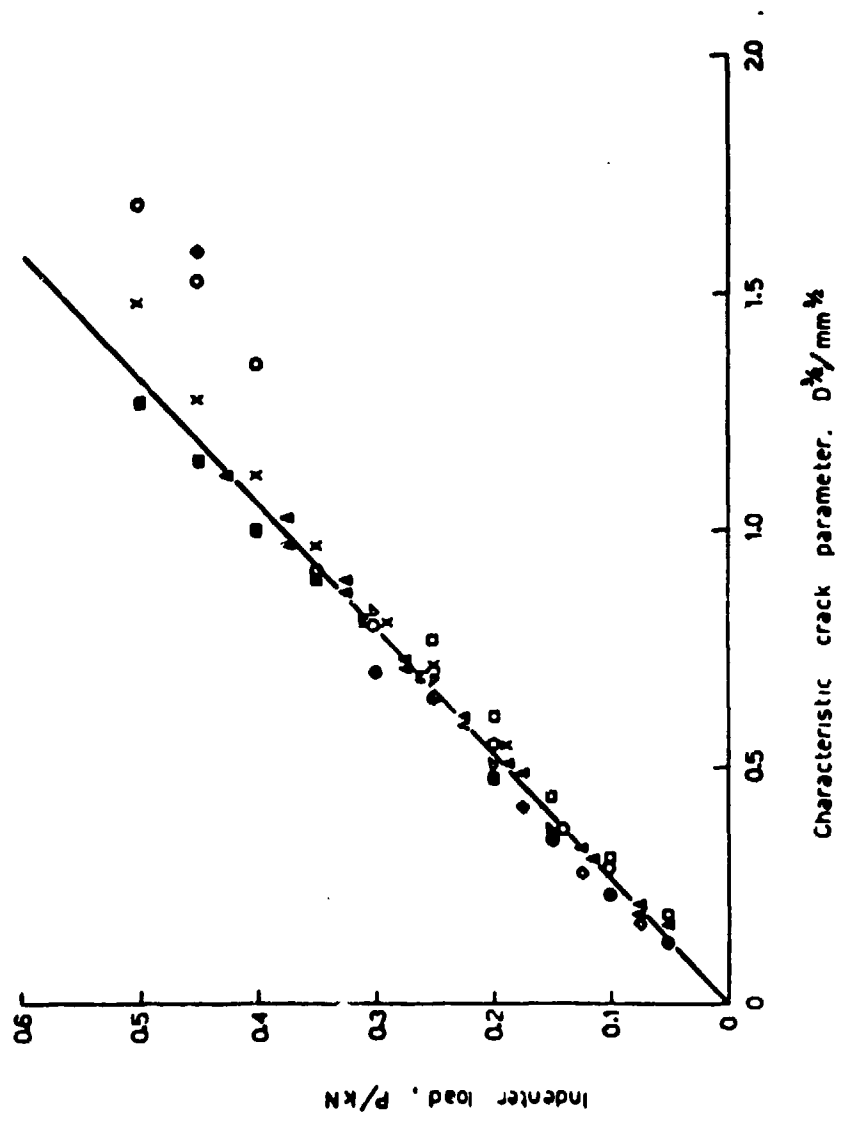
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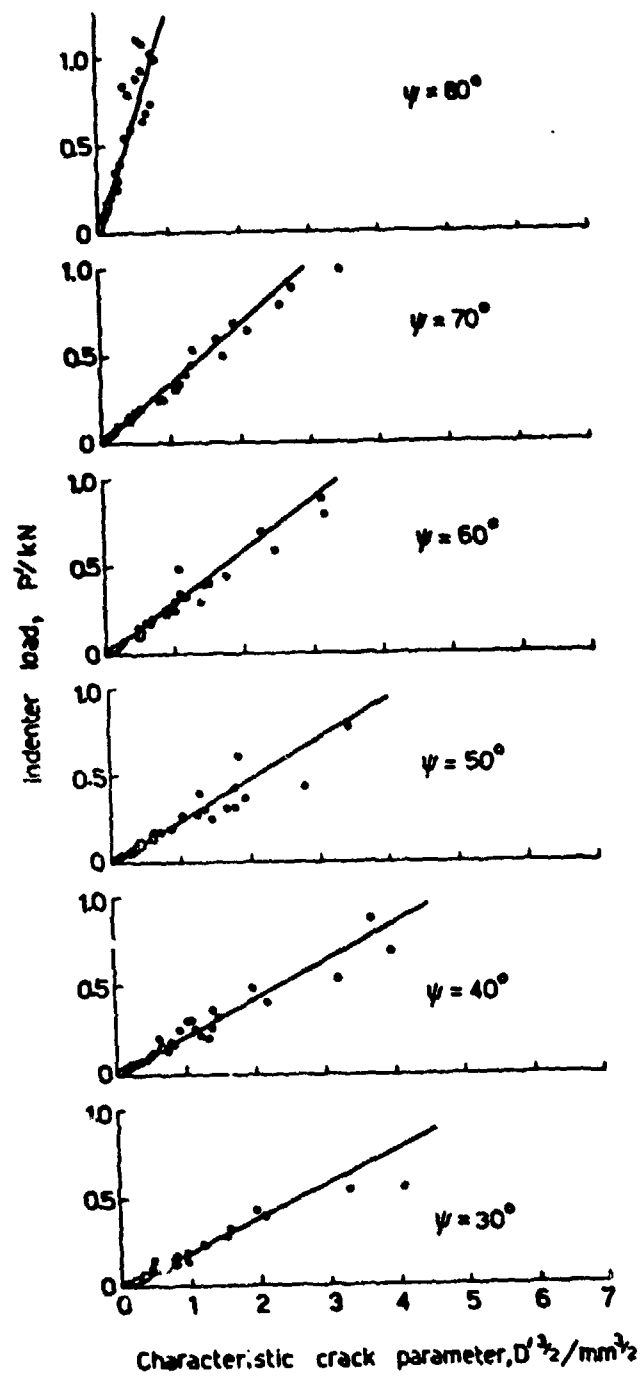


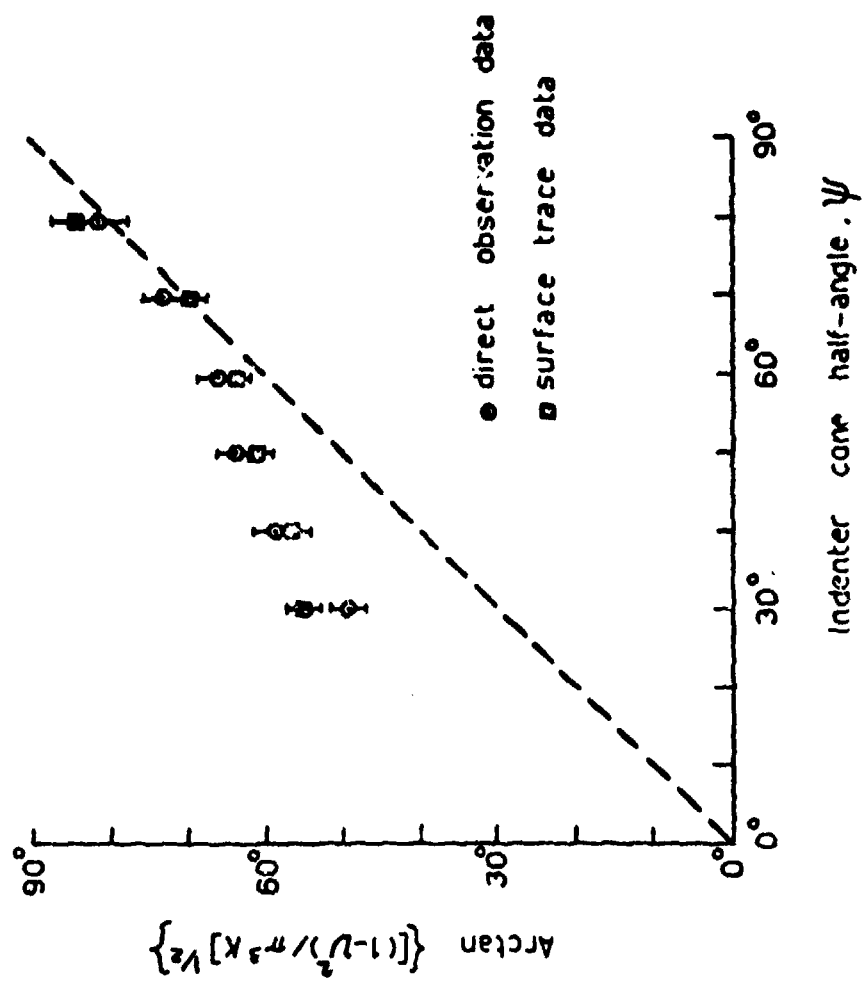




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16. ABSTRACT (A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.) A study is made of the mechanics of two basic types of indentation fracture, <i>cone cracks</i> ("blunt" indenters) and <i>median cracks</i> ("sharp" indenters). The common feature which forms the central theme in this work is that both crack types, in their well-developed stages of growth, may be regarded as essentially "penny-like". On this basis a universal similarity relation is derived for equilibrium crack dimension as a function of indentation load. Experimental measurements confirm the general form of this relation. A more detailed fracture mechanics analysis is then given, to account for additional, contact variables evident in the data. Notwithstanding certain analytical limitations, the study serves as a useful basis for investigating a wide range of contact-related problems, both fundamental and applied, in brittle solids.			
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